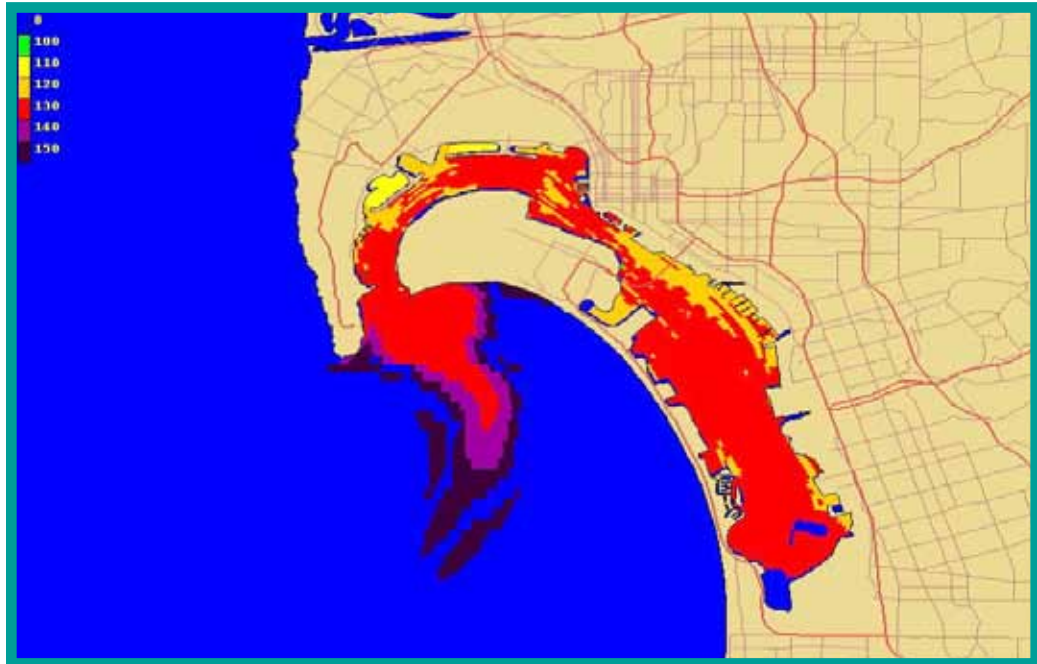


ESTCP Cost and Performance Report

(ER-0523)



Demonstration of an Integrated Compliance Model for Predicting Copper Fate and Effects in DoD Harbors

November 2008



ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 01 NOV 2008		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE Demonstration of an Integrated Compliance Model for Predicting Copper Fate and Effects in DoD Harbors				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Environmental Security Technology Certification Program (ESTCP) U.S. Department of Defense				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 49	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

COST & PERFORMANCE REPORT

Project: ER-0523

TABLE OF CONTENTS

	Page
1.0 EXECUTIVE SUMMARY	1
1.1 BACKGROUND	1
1.2 OBJECTIVES OF THE DEMONSTRATION.....	1
1.3 DEMONSTRATION RESULTS	1
1.4 IMPLEMENTATION ISSUES	3
2.0 INTRODUCTION	5
2.1 BACKGROUND	5
2.2 OBJECTIVES OF THE DEMONSTRATION.....	6
2.3 REGULATORY DRIVERS	6
3.0 TECHNOLOGY DESCRIPTION	7
3.1 TECHNOLOGY DEVELOPMENT AND APPLICATION.....	7
3.2 PROCESS DESCRIPTION	9
3.3 PREVIOUS TESTING OF TECHNOLOGY.....	10
3.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY.....	10
4.0 DEMONSTRATION DESIGN	13
4.1 PERFORMANCE OBJECTIVES	13
4.2 SELECTION OF TEST SITES/FACILITIES	13
4.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS	14
4.4 PHYSICAL SETUP AND OPERATIONS	14
4.5 SAMPLING AND MONITORING PROCEDURES.....	16
4.6 ANALYTICAL PROCEDURES.....	17
5.0 PERFORMANCE ASSESSMENT	19
5.1 PERFORMANCE DATA.....	19
5.2 PERFORMANCE CRITERIA	19
5.3 DATA ASSESSMENT	21
5.4 TECHNOLOGY COMPARISON	24
6.0 COST ASSESSMENT.....	25
6.1 COST REPORTING.....	25
6.2 COST ANALYSIS.....	28
7.0 IMPLEMENTATION ISSUES	31
7.1 COST OBSERVATIONS.....	31
7.2 PERFORMANCE OBSERVATIONS.....	31
7.3 SCALE UP.....	31

TABLE OF CONTENTS (continued)

	Page
7.4 OTHER SIGNIFICANT OBSERVATIONS.....	31
7.5 LESSONS LEARNED.....	32
7.6 END-USER ISSUES	32
7.7 APPROACH TO REGULATORY SUSTAINABLE INFRASTRUCTURE AND ACCEPTANCE	32
8.0 REFERENCES	33
APPENDIX A POINTS OF CONTACT.....	A-1

LIST OF FIGURES

	Page
Figure 1.	Demonstration of the Integrated Model for Simultaneous Evaluation of F&T and Potential Effects of Cu on a Harbor-Wide Scale..... 2
Figure 2.	Modeling Grids and Bathymetry for San Diego Bay, California and Pearl Harbor, Hawaii..... 7
Figure 3.	Schematic Diagram of the Structure of the BLM Model and the Requirements between the Existing Freshwater Model and the Emerging Seawater Model 8
Figure 4.	Comparison of Freshwater-BLM-Predicted Cu Toxicity to Measured Values in Estuaries from around the United States. 9
Figure 5.	Estimated Cu Loading to the Model Regions Designated by Chadwick et al. (2004). 15
Figure 6.	Estimated Cu Loading to Pearl Harbor, Hawaii 16
Figure 7.	Measured and Best Prediction Range for Cu Toxicity in Waters of Lake Superior..... 22
Figure 8.	Relief Predicted by the Integrated CH3D/Seawater-BLM Model with a Site-Specific WQC for San Diego Bay. 24

LIST OF TABLES

		Page
Table 1.	Performance Objectives for the Demonstration of the Integrated CH3D/Seawater-BLM in San Diego Bay, California, and Pearl Harbor, Hawaii.	13
Table 2.	Performance Data for the Demonstration of the Integrated Model.	19
Table 3.	Performance Criteria and Confirmation Methods for the Demonstration of the CH3D/Seawater-BLM.	20
Table 4.	Actual Costs Incurred in the Development and Application of an Integrated CH3D/BLM Model for San Diego Bay.	25
Table 5.	Costs Expected for the Development and Application of CH3D Model in a New Harbor.	26
Table 6.	Costs Associated with Field Development of a WER for a DoD Harbor of Similar Dimensions as San Diego Bay.	27
Table 7.	Costs Estimated for the Implementation of the Integrated CH3D/Seawater-BLM Model in Another DoD Harbor.	28
Table 8.	Summary of Costs Incurred for the Demonstration in San Diego Bay (actual), and for Implementation of Different Models in a Harbor Similar to San Diego Bay.	28

ACRONYMS AND ABBREVIATIONS

ΔC	gradient in concentration
$\mu\text{g cm}^{-2} \text{ cleaning}^{-1}$	micrograms per square centimeter per cleaning
$\mu\text{g cm}^{-2} \text{ d}^{-1}$	micrograms per square centimeter per day
$\mu\text{g L}^{-1}$	micrograms per liter, same as parts per billion
ADCP	acoustic Doppler current profiler
BLM	Biotic Ligand Model
CH3D	Curvilinear Hydrodynamics in Three Dimensions fate and transport model
CHESS	Chemical Equilibria in Soils and Solutions
CTD	conductivity, temperature, and depth
Cu	copper
Cu-ISE	copper ion-selective electrode
Cu^{2+}	free copper ion
Cu_{diss}	dissolved copper concentration
Cu_{part}	particulate copper concentration
Cu_{tot}	total copper concentration
CWA	Clean Water Act
DGPS	differential global positioning system
DoD	Department of Defense
DOC	dissolved organic carbon
DOM	dissolved organic matter
DO	dissolved oxygen
EC50	water concentration producing a toxic effect to 50% of the population
ESTCP	Environmental Security Technology Certification Program
F&T	fate and transport
ICP-MS	inductively coupled plasma with mass spectrometry
km^2	square kilometer
kg y^{-1}	kilogram per year
m	meter
M	moles per liter, a measure of concentration
MESC	Marine Environmental Survey Capability
MOS	margin of safety
mg L^{-1}	milligrams per liter

ACRONYMS AND ABBREVIATIONS (continued)

NOM	natural organic matter
NPDES	National Pollutant Discharge Elimination System
ONR	Office of Naval Research
PI	Principal Investigator
PHNS&IMF	Pearl Harbor Naval Shipyard and Intermediate Maintenance Facility
SERDP	Strategic Environmental Research and Development Program
SSC-Pacific	Space and Naval Warfare Systems Center Pacific
TMA	trace metals analyzer
TMDL	total maximum daily load
TOC	total organic carbon
TSS	total suspended solids
USEPA	U. S. Environmental Protection Agency
WER	water-effect ratio
WHAM	Windemere Humic Aqueous Model
WQC	water quality criteria
WQS	water quality standards

ACKNOWLEDGEMENTS

This Cost and Performance Report is part of Project ER-0523, Demonstration of an Integrated Compliance Model for Predicting Copper Fate and Effects in DoD Harbors, funded by the Environmental Security Technology Certification Program (ESTCP). Dr. Jeffrey Marqusee is the Program Director; Dr. Andrea Leeson is the Program Manager for Environmental Restoration. Dr. D. Bart Chadwick from SPAWAR Systems Center San Diego (SSC-Pacific) directed the project. Collaborators in this effort included Mr. Ernie Arias, Ms. Amy Blake, Dr. Ignacio Rivera-Duarte, Mr. Gunther Rosen, and Dr. Pei-Fang Wang from SSC-Pacific, Dr. Sasha D. Hafner, Mr. Paul Paquin, Dr. Adam Ryan, and Mr. Robert C. Santore from HydroQual, Inc., and Dr. WooHee Choi from San Diego State University Research Foundation. Mr. William Swietlik, Mr. Charles Delos and Mr. Luis A. Cruz from the U.S. Environmental Protection Agency (USEPA), Office of Water, Office of Science and Technology, Health and Ecological Criteria Division, provided regulatory input and support.

This project is a direct result of Project ER-1156, Fate and Ecological Effects of Copper and Zinc in Estuarine Environments: A Multi Disciplinary Program, supported by the Strategic Environmental Research and Development Program (SERDP). Dr Alberto Zirino was the original Principal Investigator (PI) in this effort, and his insight and guidance are greatly appreciated. The Office of Naval Research funded the initial effort for the measurement of copper (Cu) speciation, and Mr. Alex Lardis, the Program Manager, provided invaluable support.

We appreciate the support and input provided by Dr. Ray Arnold from the Copper Development Association, Inc., for the development of the saltwater Biotic Ligand Model, specifically by organizing meetings and communication with the USEPA.

Technical material contained in this report has been approved for public release.

This page intentionally left blank.

1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

Site-specific water quality standards (WQS) are developed in order to reach regulatory criteria appropriate for individual bodies of water. These WQS are required as the nationally suggested water quality criteria (WQC) for seawater was derived with clean coastal seawater that does not include the natural ingredients that buffer the toxic effects of contaminants. As such, federal WQC could be overprotective, enforcing effluent characteristics that are very difficult and expensive to attain. The regulatory community overcame this problem with the development of total maximum daily loads (TMDL) and water effects ratios (WER), approaches that require long-term demanding and expensive studies. In an effort to speed up the development of WQS for copper (Cu), the USEPA recently incorporated the Biotic Ligand Model (BLM) into a freshwater WQC (USEPA, 2007). This model takes into account the natural characteristics of each body of water to derive a site-specific WQS. In a similar effort, the regulatory community is supporting the development of a seawater-BLM for application in marine waters.

1.2 OBJECTIVES OF THE DEMONSTRATION

The objective is to demonstrate an integrated modeling system that provides an improved methodology for achieving compliance for Cu in Department of Defense (DoD) harbors in a manner consistent with the current regulatory framework for freshwater systems (USEPA, 2007). This system also provides a management tool for the optimization of efforts on source control, as it is robust enough for forecasting their effects on ambient Cu concentration and the potential for toxicity in DoD harbors. The integrated model consists of the Curvilinear Hydrodynamics in Three Dimensions (CH3D) and a seawater Cu toxicity model (seawater-BLM), for simultaneous evaluation of fate and transport (F&T) and potential effects of Cu on a harbor-wide scale (Figure 1).

1.3 DEMONSTRATION RESULTS

Demonstration of the integrated model in San Diego Bay and Pearl Harbor fulfilled most of the performance objectives. These objectives included a reliability parameter of explaining $\geq 60\%$ of the variability in the field data for the prediction of total Cu concentration (Cu_{tot}) and dissolved Cu concentration (Cu_{diss}). Predicted Cu_{tot} explains 61 to 94% of the variability of the measured values in both DoD harbors. In the case of Cu_{diss} , the predictive capability of the integrated model was affected by a required minimal gradient in concentration (ΔC). In the cases where there was a gradient in concentration of $0.22 \mu g L^{-1}$ or greater, the predicted values explain 68 to 92% of the variability. In contrast, in those cases where the range in Cu_{diss} was minimal (ΔC $0.009 \mu g L^{-1}$), making Cu_{diss} essentially a constant value, a case where linear regression is not applicable, the objective is not fulfilled in spite of the great similarity between the values. The performance objectives for the prediction of free Cu ion (Cu^{2+}) are adjusted for the lack of gradient. In San Diego Bay field measured Cu^{2+} was extremely stable and constant (i.e., small ΔC) and neglected the use of linear regression. The objective was therefore modified to prediction of values within an order of magnitude of measured values. This objective is fulfilled

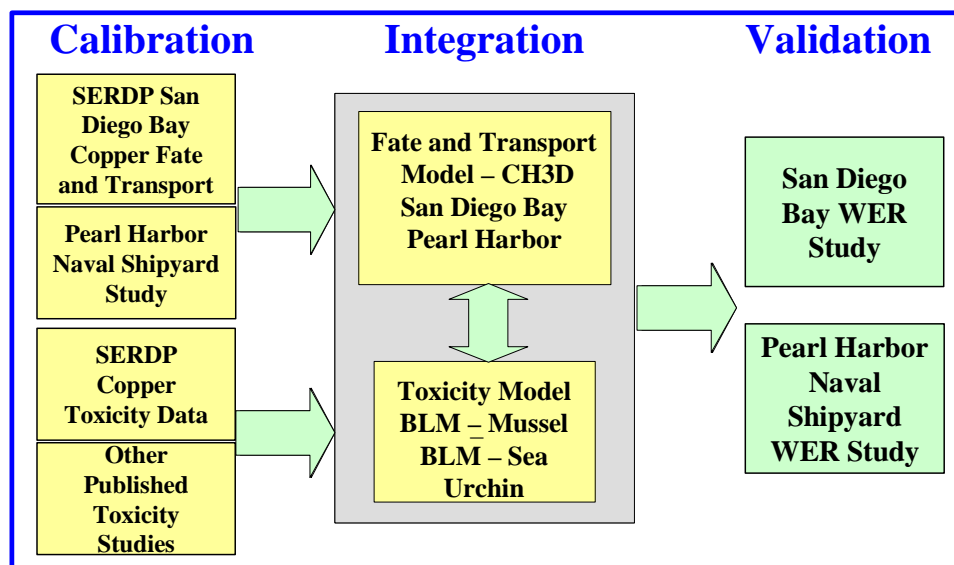
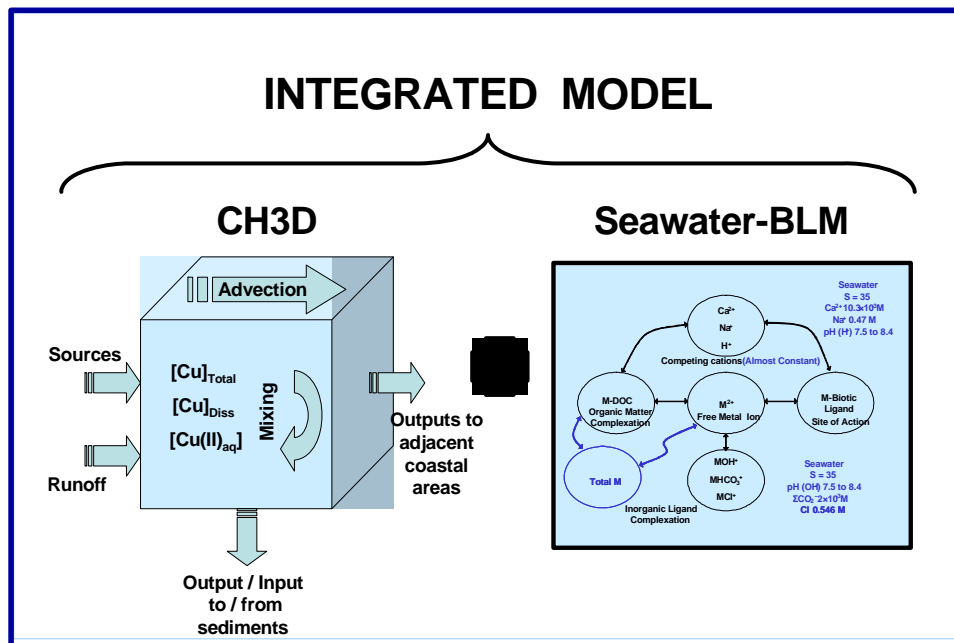


Figure 1. Demonstration of the Integrated Model for Simultaneous Evaluation of F&T and Potential Effects of Cu on a Harbor-Wide Scale.

(The model is made up by the hydrodynamic F&T model CH3D and the Cu toxicity model seawater-BLM. The figure on top explains the two separate models, and the figure in the bottom explains the process followed in the demonstration.)

for most of San Diego Bay, excluding the area by the mouth of the Bay. There are no measurements of Cu^{2+} in Pearl Harbor; therefore, there was no procedure available to evaluate the predictive capability of the integrated model there.

Regulatory use of the integrated model will be mainly on the prediction of toxicity and WQS for the whole bay. Toxicity predictions are within the expected performance criteria in both harbors, as 87% of the values predicted for both calibration and validation are within a factor of two of the measured values. Two advantages of applying the integrated model over the current approach of developing toxicity and WER studies are the spatial resolution of the predicted values and the extreme reduction in effort. The integrated model provided high-resolution (≈ 100 m) spatial distributions of toxicity and WER, which can only be developed by the inclusion of a significant number of samples when following the recommended WER approach.

Application of the integrated model for the development of WQS results in significant relief, while maintaining the intended level of environmental health. WER predicted by the integrated model for San Diego Bay and Pearl Harbor are comparable to those previously measured (Rosen et al., 2005), as 80% and 98% of the cases for both calibration and validation are within a factor of two of the corresponding measured values, respectively. A geometric mean WER of 1.48 and 1.17 were predicted for San Diego Bay and Pearl Harbor, respectively, which are within the range previously reported. Application of a mean WER for each area in San Diego Bay results in significant relief, with an average WQS of $5.0 \mu\text{g L}^{-1}$ for the whole bay.

1.4 IMPLEMENTATION ISSUES

Implementation of the integrated model in a new harbor will result in lower costs than those required for existing processes. The costs for this demonstration of the integrated model are compared to the costs expected from the individual implementation of a WER and an F&T model in a harbor of similar dimensions and characteristics as San Diego Bay. While this comparison is justified by the fact that both processes are required to provide information similar to that generated by the integrated model, the costs predicted for implementation of these processes was simplified to some degree. Moreover, a significant increase in effort should be expected in order for these processes to provide the same quality on spatial information, and capability for forecasting effects. The cost of the demonstration in San Diego Bay was \$580,000, which is \$250,894 more than the costs estimated for implementation of a WER and a CH3D (\$329,106). However, implementation of the integrated model in a new harbor is estimated at \$189,368. This will provide better temporal and spatial resolution, and forecasting capability of source controls.

This demonstration contributes to the transition of this technology to the user community by providing a clear example of implementation at real-world DoD sites. Critical aspects of this contribution include development and refinement of the BLM for sensitive saltwater toxicity endpoints, and implementation of USEPA guidance for TMDL and site-specific WQS within a rigorous numerical modeling framework for Cu and eventually other metals.

This page intentionally left blank.

2.0 INTRODUCTION

2.1 BACKGROUND

There is a growing DoD requirement for the development of site-specific WQS and scientifically defensible TMDL to achieve compliance of Cu point source and nonpoint source discharges to harbors. Cu is one of the ubiquitous contaminants found in industrial and nonpoint source effluents that enter the marine environment, including those from DoD activities, such as shipyards, stormwater, and ships (Nriagu, 1996; Johnson et al., 1998; Seligman and Zirino, 1998; Zirino and Seligman, 2002). Because of its wide use as a biocide in antifouling coatings and in piping systems, Cu is a particularly prevalent contaminant in and around DoD pier areas, shipyards, marine facilities, and harbors. Copper in the marine environment is regulated under the Clean Water Act (CWA) at levels that generally do not recognize site-specific complexation of copper that controls toxicity (USEPA, 1997). Strict application of copper WQS at DoD facilities without accounting for site-specific factors has led to difficulties in compliance with the resulting discharge permits and disproportionate cost requirements for containment and/or treatment systems.

Development of site-specific WQS and TMDL is closely linked. Site-specific WQS dictate the understanding of copper bioavailability in local waters, while TMDL require the understanding of loading terms, mass balance, and assimilation capacity of a particular water body (USEPA, 1999a). TMDL actions are generally triggered when a water body is designated as impaired based on ambient water concentrations exceeding the WQS. Thus, the development of site-specific WQS can strongly influence the designation of impairment and the subsequent requirement for TMDL. For example, in San Diego Bay, ambient copper concentrations approach or exceed the USEPA WQC and the state WQS ($3.1 \mu\text{g L}^{-1}$, USEPA, 1997; Katz, 1998; Chadwick et al., 2004; Blake et al., 2004); however, toxicity studies suggest that ambient concentrations would not result in toxicity or exceed a site-specific WQS after the application of a WER (Rosen et al., 2005). A different situation occurred in Pearl Harbor, where ambient copper concentrations are well below the WQC ($0.62 \pm 0.25 \mu\text{g L}^{-1}$, average ± 1 standard deviation) (Earley et al., 2007); but, discharges at the Pearl Harbor Naval Shipyard and Intermediate Maintenance Facility (PHNS&IMF) were regulated to a WQS of $2.9 \mu\text{g L}^{-1}$. Implementation of actions to derive WQS for Pearl Harbor demonstrated that that level of regulation was overprotective (Earley et al., 2007). Implementation of a site-specific WQS in both cases could reduce the likelihood of TMDL actions.

The present USEPA WQC justifiably fulfill their mission of protecting the environment but generally do so from a scientific basis that does not account for site-specific factors that regulate bioavailability and toxicity, and thus are often overprotective (Seligman and Zirino, 1998; Zirino and Seligman, 2002) relative to the level of protection intended by the guidelines (Stephan et al., 1985). In recognition of this conservatism, the effects of copper speciation and bioavailability in seawater are addressed indirectly by the regulatory community via the adoption of a number of mechanisms. These mechanisms include using Cu_{diss} rather than total recoverable copper (Cu_{tot}) concentration (Metals Translator) (USEPA, 1996), and using WER (USEPA, 2001). This is a multiplier of the national ambient WQS, which is derived from the ratio between the toxicity observed in the regulated body of water and that from laboratory water used for the development of the federal WQC. While these empirical strategies provide one pathway for implementation of site-specific WQS and discharge permits, they are often expensive to employ and do not

provide a strong technical basis for addressing the complete range of factors that influence transport, fate, and effects. As an alternative, copper speciation and bioavailability in freshwater systems have been addressed by using the BLM (Di Toro et al., 2001; Santore et al., 2001; USEPA, 2007) to derive a site-specific WQC. The BLM, which is based on evidence that mortality occurs when the metal-biotic ligand complex reaches a critical concentration, considers site-specific water quality characteristics to predict this critical concentration. The BLM-based approach has the potential to be more cost effective and easier to implement than the WER approach as a way to evaluate site-specific WQS for metals in seawaters.

2.2 OBJECTIVES OF THE DEMONSTRATION

Our objective is to demonstrate an integrated modeling system that will provide an improved methodology for achieving compliance for copper in DoD harbors (i.e., developing TMDL, site-specific WQS, and WERs) in a manner consistent with the current regulatory framework recently released for copper in freshwater systems (USEPA, 2007). The proposed system will also provide a management tool for the optimization of efforts on source control, as it will be robust enough for forecasting effects on copper concentration and the potential for toxicity in the harbor because of these efforts. The integrated model will include a hydrodynamic F&T algorithm (i.e., CH3D model) and a copper toxicity submodel (i.e., seawater-BLM) for simultaneous evaluation of F&T and potential effects of copper on a harbor-wide scale. This integrated modeling system was demonstrated by applying it to San Diego Bay, California, and Pearl Harbor, Hawaii. Results of this demonstrated technology could reduce control and treatment costs through more appropriate, site-specific WQS and discharge limits while maintaining the level of environmental protection required by current regulation. In addition, the development of copper toxicity parameters for the implementation of the seawater-BLM should provide WQS that better represent the actual environmental characteristics of the harbor and reduce requirements for costly empirical studies.

2.3 REGULATORY DRIVERS

Federal regulations that motivate the development of site-specific WQS and scientifically defensible TMDL include the WQC (USEPA, 2007) and the National Pollutant Discharge Elimination System (NPDES) program. DoD drivers include the following environmental requirements from the U.S. Navy Pollution Abatement Ashore program¹: 2.II.02.e, Improvements in Three Dimensional Models of Contaminant Fate and Effects in the Marine Environment; 2.II.02.b, Improved Field Analytical Sensors, Toxicity Assays, Methods, and Protocols to Supplement Traditional Sampling and Laboratory Analysis; 2.II.01.k, Control/Treat Nonpoint Source Discharge; and 2.II.01.q, Control/Treat Industrial Wastewater Discharges.

¹ http://www.paa.navy.mil/PAAEnvironmentalRqmnts_Archive.aspx

3.0 TECHNOLOGY DESCRIPTION

3.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

The demonstrated technology is a direct transition from the Strategic Environmental Research and Development Program (SERDP) project ER-1156. This technology integrates two primary components (Figure 1): 1) the CH3D model for tracking sources and simulation of F&T and distribution of Cu and 2) a seawater-BLM toxicity model for simulation of chemical speciation, competition, exposure, and response of sensitive marine organisms to the species of Cu present, including Cu^{2+} .

Fate and Transport Modeling. CH3D is a boundary-fitted finite difference, z-coordinate F&T model developed at the U.S. Army Corps of Engineers Waterways Experiment Station (Johnson et al., 1991) to simulate physical processes in bays, rivers, lakes and estuaries (Wang and Martin, 1991; Wang, 1992; Wang and McCutcheon, 1993; Johnson et al., 1995; Wang et al., 1997, 1998). The model simulates hydrodynamic currents in four dimensions (x, y, z and time) and allows for the prediction of F&T of metals, fecal coliforms and other contaminants under the forcing of tides, wind and freshwater inflows (Sheng et al., 1991; Wang and Richter, 1999). It has been applied to a number of Navy-USEPA joint projects, including the Environmental Investment TMDL project for Sinclair Inlet, Washington (Wang and Richter, 1999), the Uniform National Discharge Standards Program for ship discharges in Norfolk, Virginia, and the NPDES permit study for PHNS&IMF. The grid for San Diego Bay covers an area of approximately 215 km^2 , with about 7,000 grid elements, and a resolution of approximately 100 meters (m); the grid for Pearl Harbor covers an area of 20.4 kilometers squared (km^2), with 2,342 grid elements, with a resolution from about 50 to 200 m (Figure 2). CH3D allows for enhancements for specific applications; for this study, the enhancement was a seawater-BLM.

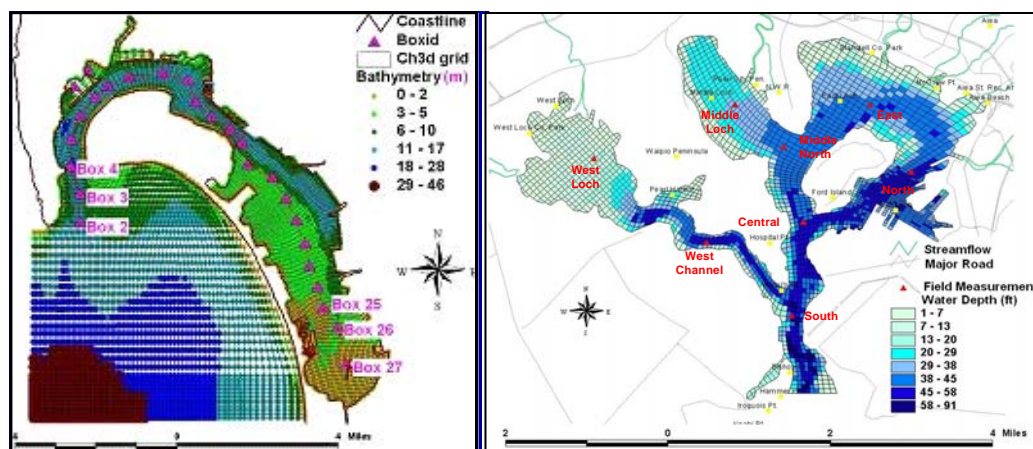


Figure 2. Modeling Grids and Bathymetry for San Diego Bay, California (left) and Pearl Harbor, Hawaii (right).

Toxicity Modeling. The BLM of metal toxicity to aquatic organisms is based on the evidence that mortality occurs when a predefined metal-biotic ligand complex reaches a critical concentration (Di Toro et al., 2001; Santore et al., 2001). It is convenient to consider the site of action of metal toxicity as a biotic ligand and, in the case of freshwater fish, the proximate site of action of toxicity for metals such as Cu or silver, is the gill (Wood, 2001). It is similarly

assumed for other freshwater and saltwater organisms, as a first approximation, that analogous physiological processes are involved in ionoregulation and can be modeled with a similar framework. The biotic ligand interacts with the metal ions in solution, and the amount of metal that it binds is determined by a competition for metal ions with other aqueous ligands (Figure), particularly dissolved organic matter (DOM), and the competition for the biotic ligand between the bioavailable forms of the stressor metal and the other cations in solution.

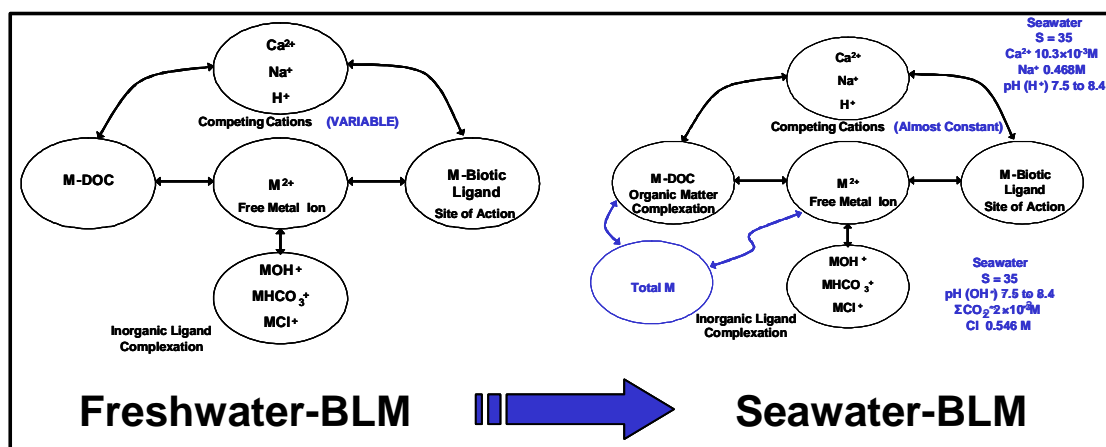


Figure 3. Schematic Diagram of the Structure of the BLM Model and the Requirements between the Existing Freshwater Model (left side) and the Emerging Seawater Model (right side).

The BLM for freshwater organisms has been well documented and tested (Figure 3, left flow chart). The model is an adaptation of the free ion activity model, which posits that the free metal ion is correlated to toxicity (Morel, 1993; Campbell, 1995). The model is implemented using a chemical description of metal-DOM interactions developed for the Windemere Humic Aqueous Model (WHAM) (Tipping, 1994), with the WHAM formulation simulated within the Chemical Equilibria in Soils and Solutions (CHESS) model (Santore and Driscoll, 1995). It has been applied for Cu, zinc, cadmium, lead, and silver for fish and invertebrates in freshwater and for Cu, using larval *Mytilus spp.* (mussel), in saltwater. The BLM is amenable for use in the context of TMDL and regional risk assessments and within a probabilistic framework. As a result of extensive calibration and validation efforts, as well as the scientifically rigorous conceptual basis for the model, the Cu BLM has been incorporated into a freshwater WQC (USEPA, 2007).

Previous efforts to apply the freshwater-BLM to marine organisms provided promising results for estuarine conditions, but not for marine conditions. Both of these results are shown in Figure 4, where the freshwater-BLM predicted Cu toxicity to *M. edulis* (blue or bay mussel) in waters from estuaries around the United States is compared to measured Cu toxicity. In this figure, a solid line indicates the response for perfect agreement, and dashed lines indicate the area of agreement within a factor of two. The model predictions for a number of estuaries, including San Francisco Bay, Puget Sound, Galveston Bay, and Narraganset Bay are within the factor of two accepted by USEPA for the freshwater BLM (Erickson et al., 1987; USEPA, 2007). However, these efforts to apply the model to marine organisms used biotic ligand parameters that were developed from freshwater chemical speciation and biological uptake and response for freshwater fish. This extrapolation from freshwater to marine systems was necessary due to the lack of good experimental data quantifying Cu speciation, accumulation and response for marine

water and organisms. The use of the freshwater model resulted in a reproducible bias when applied to marine waters collected in open ocean waters. The results for Pacific Ocean samples (blue squares) in Figure 4 indicate that the freshwater model consistently predicted Cu EC50 values that were too low, compared with measured Cu toxicity in these samples.

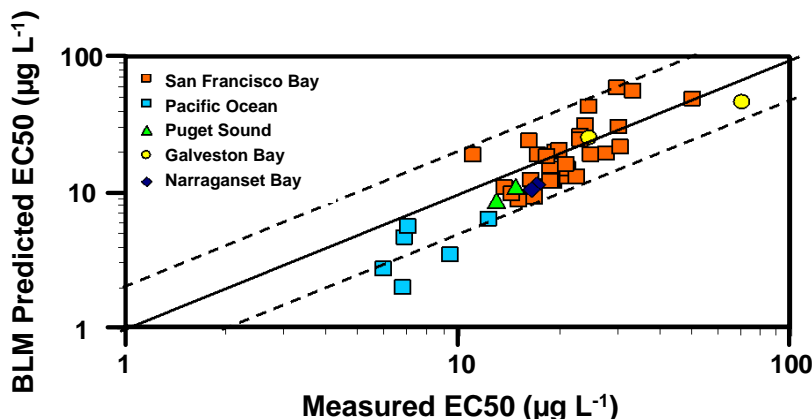


Figure 4. Comparison of Freshwater-BLM-Predicted Cu Toxicity to Measured Values in Estuaries from around the United States.

(The solid line represents the one to one ratio, and the broken lines encompass a factor of two.)

As indicated in the conceptual BLM model shown in Figure 3, conditions for freshwater organisms (left panel) can be extrapolated to marine organisms (right panel) by considering differences in the chemical nature of the exposure conditions and how those differences relate to Cu speciation, organic matter interactions, salinity (ionic strength) and organism physiology. In this project the seawater-BLM benefited from independent data collected for marine waters and organisms to develop appropriate parameter values in the development of a seawater-BLM. The resulting implementation of the seawater-BLM does not use empirical correlations, but instead it is based on a mechanistic thermodynamic description of seawater-specific metal-natural organic matter (NOM) binding, and organism-specific uptake and response. This description, including reaction stoichiometry and thermodynamic constants, was developed using measured Cu speciation from titrations in San Diego Bay water samples that were done as part of SERDP Projects ER-1156 and ER-1157 and were substantiated by similar Cu titrations that were done in water samples from Pearl Harbor as part of the Copper Water Compliance Studies at PHNS&IMF (Earley et al., 2007). Larval accumulation and response studies with sensitive marine organisms were done as part of the demonstration of the integrated model in San Diego, California, the first demonstration of this project, in order to provide realistic seawater toxicity parameters for the seawater-BLM that do not rely on empirical correlations extrapolated from freshwater. The seawater-BLM was re-formulated to use these reactions and parameters and was used to simulate Cu chemistry, bioavailability, and toxicity for comparison with measurements in Pearl Harbor for field validation.

3.2 PROCESS DESCRIPTION

The initial demonstration in San Diego Bay included preliminary calibration and validation of CH3D and seawater-BLM. It also included laboratory studies on Cu accumulation by larvae of two sensitive organisms for the development of the seawater-BLM. Once these models were calibrated and validated, two consecutive approaches were followed for the integration of CH3D

with the seawater-BLM. The first approach was by means of an external integration, where the output of each model was used as feedback into the other model, with each model running separately. Once the external integration was validated, the two models were internally integrated into a unified model, with concurrent processing of data and output. This final integrated model was also calibrated and validated following the use of existing data. The integrated model was used throughout the demonstration in Pearl Harbor.

At each harbor, the field data was divided into two groups, one for calibration and the other for validation. For San Diego Bay, data for calibration is from August 30, 2000 (SD26), January 30, 2001 (SD27), February 27, 2002 (SD33), and May 14, 2002 (SD35); and data for validation is from May 11, 2001 (SD31) and September 19, 2001 (SD32). For Pearl Harbor, the data for calibration is from March 15-18, 2005 (Event 1), May 15-19, 2006 (Event 4), and from January 23-27, 2006 (Event 3), the data from October 18-20, 2005 (Event 2) was used for validation but only with parameters from events 1 and 4, as January 23-27, 2006 (Event 3) is considered different since it is the only one for the wet season.

3.3 PREVIOUS TESTING OF TECHNOLOGY

The demonstration represents a natural extension of efforts that have been supported by the Office of Naval Research (ONR), SERDP, the Water Environment Research Federation, HydroQual, Inc., and others that have been recently summarized in a review document developed from the 2001 ONR Copper Workshop (Zirino and Seligman, 2002).

Field data developed for the SERDP Project ER-1156 was used for the development of the CH3D model in San Diego Bay. These data have been documented in a series of recent publications, including a description of the field program (Blake et al., 2004); methods (Rivera-Duarte and Zirino, 2004); mass balance (Chadwick et al., 2004); WER application (Rosen et al., 2005); and bioaccumulation factors (Rosen et al., 2008). Field data for the demonstration at Pearl Harbor is a direct result of the Copper Water Compliance Studies at PHNS&IMF (Earley et al., 2007). Development of the BLM, primarily for application to freshwater species, has been documented in a series of publications including a historical overview (Paquin et al., 2002a); technical basis (Di Toro et al., 2001); application to acute Cu toxicity in freshwater fish and *Daphnia* (Santore et al., 2001); and application to silver toxicity in fish and invertebrates (Paquin et al., 2002b, 2007; Bielmyer et al., 2007). USEPA has recently proposed using the BLM in freshwater as an alternative to the WER method currently used (USEPA, 2007).

3.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

One of the advantages of the integrated model is that it is a more efficient approach than the traditional measurement program approach since the initial costs of toxicity testing, seawater-BLM calibration, and integration of the seawater-BLM with CH3D will not have to be repeated for future applications in other DoD harbors. The more expensive traditional technologies for regulatory purposes and estimation of Cu loads and toxicity in harbors include environmental monitoring and development of WER, TMDL, and mass balance models. Another approach for regulatory purposes is the implementation and measurement for load scenarios; however, this approach does not always consider the natural physical, toxicological, and chemical characteristics of harbors, factors that are fully considered in the integrated model. The integrated model also has advantages to the regulatory approach of application of total Cu

concentration (Cu_{tot}) and Cu_{diss} -based standards. Adequate scientific evidence has shown that the free ion is the principal parameter for evaluation of toxic effects in aquatic environments and the integrated model intrinsically relates toxicity to the free ion concentration. Another advantage is that the model should be relatively easy to implement in other harbors, where it could be applied with an optimized approach to data requirements. As CH3D is a model commonly used by the regulated community, the implementation and use of the integrated model should be relatively easy. Another advantage of CH3D is its capability for enhancement; this is for the inclusion of subroutines for specific purposes, and the seawater-BLM was relatively easy to integrate into the model. An advantage of the integrated model for management is that it provides predictive capability for pollution control scenarios, including optimized effluent management. It will also allow for the assessment of load allocation scenarios required for a TMDL regulatory approach. The integrated model also has the advantage of providing the basis/framework for the assessment of the F&T and effects of other contaminants in DoD harbors.

The limitations of the integrated model are related to the range of environmental conditions in DoD harbors. The model was calibrated for only two saltwater species (i.e., the larval life stage of the blue mussel and purple sea urchin), and while these species are among those most sensitive to Cu, there could be other species that are more significant for other harbors. It should be noted, however, that the larval blue mussel is among the species included in this analysis and this is the most sensitive organism to Cu in the USEPA marine database. While it is true that other DoD harbors may have other marine organisms that have not been tested in this analysis, the inclusion of the blue mussel in this work makes the calibrated model generally applicable as an alternative approach for deriving site-specific WQC in all marine environments.

A parameter considered of supreme importance for the regulation of toxicity in harbors is dissolved organic carbon (DOC) (Arnold, 2005; Arnold et al., 2006). As the quantity and quality of DOC could vary spatially and temporally in any harbor, the model will require some calibration and validation in any other harbor. The natural variation of environmental parameters will require some data collection and/or estimation of unmodeled parameters required for the integrated model. A limitation to the integrated model could arise in those small harbors or limited areas of impairment where the costs of calibration and validation of the model outweigh those for traditional assessments.

Probably the most important limitation at this time is that regulatory acceptance of the seawater-BLM is still in process. Results from the final calibration and validation of the seawater-BLM were presented to personnel from the USEPA, Office of Water, Office of Science and Technology, Health and Ecological Criteria Division on April 14, 2008. At this meeting, it was accepted that the seawater-BLM is ready for inclusion for full-strength seawater regulation. The final procedures for its inclusion were completed in November 2008. A draft document for the inclusion of the seawater-BLM for regulatory use could be achieved by 2010.

This page intentionally left blank.

4.0 DEMONSTRATION DESIGN

4.1 PERFORMANCE OBJECTIVES

The performance objectives for this demonstration are shown in Table 1.

Table 1. Performance Objectives for the Demonstration of the Integrated CH3D/Seawater-BLM in San Diego Bay, California, and Pearl Harbor, Hawaii.

Type of Performance Objective	Primary PERFORMANCE CRITERIA	Expected Performance (Metric)	Actual Performance Objective Met in San Diego Bay?	Actual Performance Objective Met in Pearl Harbor?
Quantitative	1. Comparison between modeled and measured Cu_{tot}	The model should explain $\geq 60\%$ of the variance in the Cu_{tot} field data.	Yes	Yes
	2. Comparison between modeled and measured Cu_{diss}	The model should explain $\geq 60\%$ of the variance in the Cu_{diss} field data.	Yes	Yes
	3. Comparison between modeled and measured free Cu ion (Cu^{2+})	The model should predict values in the same order of magnitude as the Cu^{2+} field data.	Yes	Not measured
	4. Comparison between modeled and measured toxicity	The model should predict the field data for toxicity within a factor of two.	Yes	Yes
	5. Comparison between modeled and measured WER	The model should predict the WER field data within a factor of two.	Yes	Yes
Qualitative	1. Model stability	The integrated model should run 95% of the time with no interruptions.	Yes	Yes
	2. Computational time	The integrated model should run $\geq 30\%$ faster than running the CH3D and the seawater-BLM models alternatively.	Yes	Yes

4.2 SELECTION OF TEST SITES/FACILITIES

There are two criteria for selection of the harbors— 1) they must sustain a significant use by the DoD, and 2) the required environmental information should be available. San Diego Bay fulfills these criteria as it is heavily used by the Navy, and the required information is available. Navy bases located in the San Diego Bay area include: Naval Air Station, North Island; Naval Amphibious Base, Coronado; Imperial Beach; Fleet Anti-Submarine Base; Naval Station San Diego, Submarine Base, Old Town Campus; Broadway Complex in San Diego; and Naval Medical Center, Balboa. The information required for San Diego Bay is in part a direct result of SERDP Project ER-1156. Pearl Harbor also fulfills these criteria. It is heavily used by the DoD, with installations including Naval Station Pearl Harbor, PHNS&IMF, Naval Submarine Base, Hickam Air Force Base, Tripler Medical Center, Ford Island, Camp Smith Marine Corps Base, Manama Pearl City, Naval Computer and Telecommunications Area Master Station, Pacific, and

the Naval Magazine West Loch. The required information is available for Pearl Harbor as direct result of the Copper Water Compliance Studies at PHNS&IMF performed to develop site-specific water quality objectives, in support of NPDES permit negotiations (Earley et al., 2007). The information includes a geographical and temporal description of environmental conditions, Cu chemical speciation, Cu toxicity, and WER calculations in both harbors.

4.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS

San Diego Bay is an ideal site for the demonstration and validation of this model, as hydrological and chemical characteristics in the bay are at a relative steady state and well constrained. Hydrographic conditions are a minimal temporal change in salinity distributions, with predominantly hypersaline conditions in the back of the bay (Chadwick and Largier, 1999a, 1999b; Blake et al., 2004). The quasi steady-state hydrographic conditions are coupled with a long-term persistence of temporal and spatial distributions of Cu_{tot} and Cu_{diss} in San Diego Bay that have been confirmed by a suite of studies (Zirino et al., 1978; Flegal and Sañudo-Wilhelmy, 1993; Esser and Volpe, 2002; Blake et al., 2004; Chadwick et al., 2004). Coupled to these relative constant conditions, there are no wastewater point sources to the Bay, and the recognized point and nonpoint sources are well studied (Johnson et al., 1998; Schiff and Diehl, 2002; Valkirs et al., 2003; Schiff *et al.*, 2004; Chadwick et al., 2004). The bay has been extensively studied for the fate and effects of Cu as part of SERDP Projects CP-1156, CP-1157 and CP-1158. As a result of these studies, the information on sources, mass-balance, partitioning rates and toxic effects is readily available (Blake et al., 2004; Chadwick et al., 2004; Shafer et al., 2004; Boyd et al., 2005; Rivera-Duarte et al., 2005; Rosen et al., 2005). One data gap for development of the seawater-BLM was the Cu uptake by larvae of sensitive marine organisms.

Pearl Harbor is located on the south-central side of the Island of Oahu. It is a large estuarine environment composed of three larger lochs (East, Middle and West) and one smaller loch (Southeast) that are all separated by a narrow channel to the open ocean. The surrounding area is one of the most densely populated areas in Hawaii. There are several highly urbanized streams that flow into Pearl Harbor, including the Halawa, Aiea, Kalauao, Waimalu, and Waimanu streams that empty into the East Loch; the Waiawa stream that empties into the Middle Loch; and the Kapahahi, Waikale, and Honouliuli streams that empty into the West Loch. The marine waters of Pearl Harbor are listed as impaired due to exceeding the water quality standards for nutrients, turbidity, suspended solids, and polychlorinated biphenyls (Hawaii State Department of Health, 2004). In contrast, Cu_{diss} in Pearl Harbor have been reported to be low throughout most of the year, with an overall average of $0.62 \pm 0.25 \mu g L^{-1}$ (\pm one standard deviation) (Earley et al., 2007). In spite of the fact that seasonal rain events can significantly affect these conditions, with the highest Cu concentrations measured during a stormwater event, toxicity was undetected in samples of the harbor (Earley et al., 2007).

4.4 PHYSICAL SETUP AND OPERATIONS

The main source of Cu to San Diego Bay is leaching from antifouling paint. Recently, Chadwick et al. (2004) updated the estimated Cu inputs to San Diego Bay to a good degree of certainty. Their estimates are based on compilations on Cu releases from civilian and Navy hull coating leacheates, civilian and Navy hull cleaning, other ship discharges (e.g., cooling water), point-source discharges, stormwater runoff, and atmospheric deposition (Johnson et al., 1998; PRC, 1997) that were updated to account for recent improvements in estimates for various input rates and to incorporate estimates for particulate Cu (Cu_{part}) (Figure 5). Input rates were modified in

response to the compilation of measurements from Seligman et al. (2001), and Valkirs et al. (2003). Following these measurements, the estimate for Navy hull coating leaching rates were updated to $3.8 \mu\text{g cm}^{-2} \text{d}^{-1}$, and civilian and commercial hull leaching rates were updated to $8.2 \mu\text{g cm}^{-2} \text{d}^{-1}$, instead of $17 \mu\text{g cm}^{-2} \text{d}^{-1}$ previously used for both of these releases (Johnson et al., 1998). The input of Cu_{diss} from civilian hull cleaning was updated based on a discharge rate of $6 \mu\text{g cm}^{-2} \text{cleaning}^{-1}$ (Schiff and Diehl, 2002). Navy and civilian hull cleaning inputs for Cu_{part} were calculated from the dissolved estimates by applying the particulate to dissolved ratio reported by USEPA (1999b). Atmospheric and direct rainfall inputs were calculated following PRC (1997), but were apportioned to surface area. Stormwater inputs of Cu_{diss} were updated to use measured event mean concentrations for all available watersheds with the remaining areas calculated following the simple model method described by Johnson et al. (1998). Cu_{part} loading from base flow and stormwater were calculated using the particulate:dissolved ratio for event mean concentrations reported by Woodward-Clyde (1996). The results of this analysis indicate Cu_{tot} loadings of about $20,400 \text{ kg y}^{-1}$ and $22,000 \text{ kg y}^{-1}$ for dry weather and wet weather conditions respectively, and that releases from antifouling paint are the main source of Cu, accounting of up to 65%, within the Bay (Chadwick et al., 2004) (Figure 5). The analysis also indicated that the distribution of Cu sources in the bay is localized. The distribution of vessels seems to be the main factor affecting the distribution of Cu sources in the bay (Figure 5). While the outer part of the Bay (boxes 1 to 17) is dominated by pleasure boat sources, the inner part (boxes 18 to 27) is dominated by ship (i.e., commercial and military) sources.

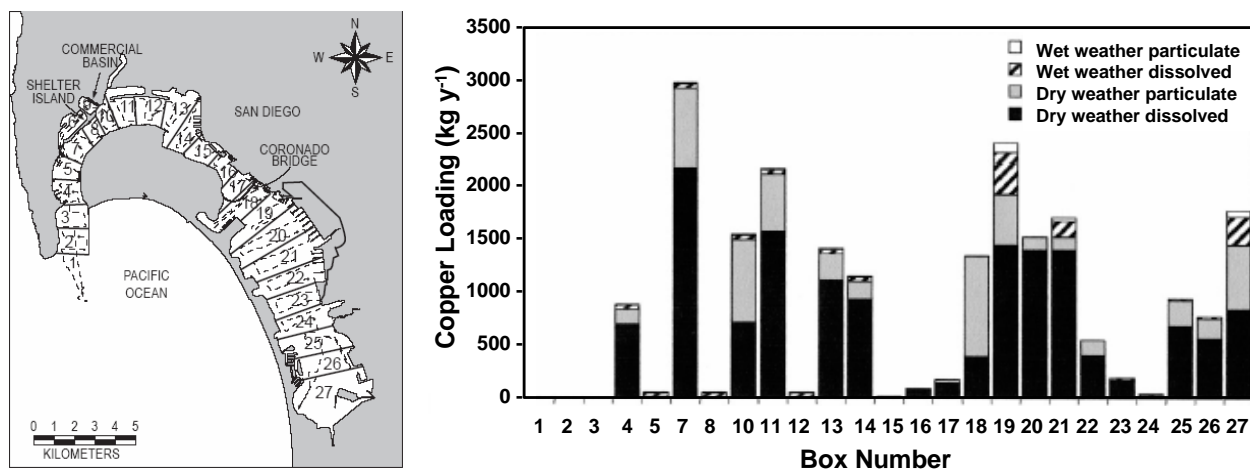


Figure 5. Estimated Cu Loading to the Model Regions Designated by Chadwick et al. (2004).

(The map [left] with the boxes and the transit path [broken lines] in San Diego Bay, California, and the estimated Cu loading at each box [right].)

The main sources of Cu to Pearl Harbor are from ship discharges and leaching from antifouling paint. Estimates of Cu inputs to Pearl Harbor were updated from those from Johnson et al. (1998), which are based on compilations of Cu releases from civilian and Navy hull coating leacheates and hull cleaning, as well as from other ship discharges (e.g. cooling water), point-source discharges, stormwater runoff, and atmospheric deposition. The updated values (Figure 6) account for recent improvements in measurements for various input rates (Seligman et al., 2001; Valkirs et al., 2003). Following these new measurements, the estimates for Navy hull coating leacheates were updated by applying a $3.8 \mu\text{g cm}^{-2} \text{d}^{-1}$, while the civilian and commercial

hull leacheates were updated using $8.2 \mu\text{g cm}^{-2} \text{d}^{-1}$, instead of $17 \mu\text{g cm}^{-2} \text{d}^{-1}$ previously used for both of these releases (Johnson et al., 1998).

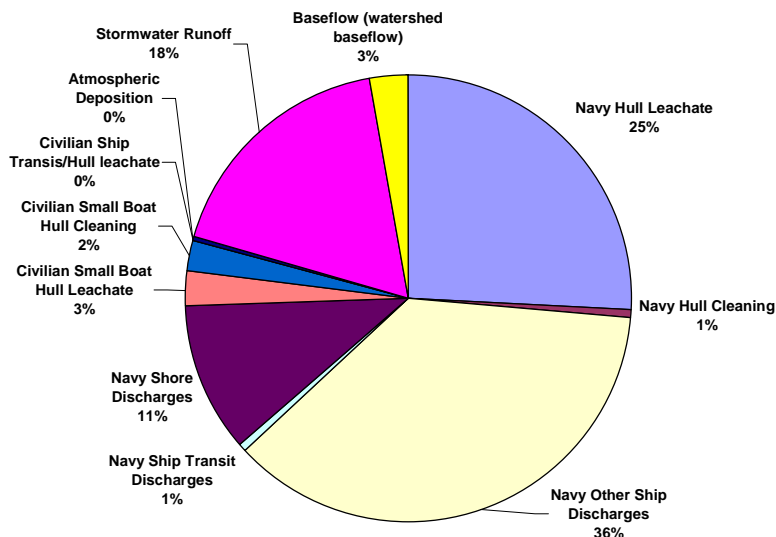


Figure 6. Estimated Cu Loading to Pearl Harbor, Hawaii.
(data updated from Johnson et al. [1998].)

4.5 SAMPLING AND MONITORING PROCEDURES

Data developed for six sampling events as part of the SERDP Project CP-1156 were used for San Diego Bay. Only the samples for the studies on Cu larval bioaccumulation were collected as part of this project. The plan for the six sampling events in SERDP CP-1156 was developed on the basis of modeling and environmental factors. Modeling factors include the partition of San Diego Bay into the 27 boxes described in the map in Figure 5. The dimensions of each box were designed on the basis of the modeling boundaries required for that project. Environmental factors affecting the sampling plan included the geographical distribution and seasonal variation of environmental parameters. Sampling included the whole extension of the bay to capture the complete extent of spatial variation. It also included the two main seasons observed, which are the dry season characterized by higher salinities within the bay, and the wet season with a decrease of salinity going into the head of the bay.

Some of the parameters were measured on transit, others from subsamples and grab samples. Each sampling event consisted of transiting from the mouth to the head of the bay in one day. The transect layout included two transverse legs within each of the 27 predefined sampling boxes (Figure 5). During transit continuous measurements were done, and composite and grab samples were collected with the Marine Environmental Survey Capability (MESC) real-time system with the use of both a towed sensor package and a trace metal clean Teflon® seawater flow-through system. Sensors in the towed package included a conductivity, temperature, and depth (CTD) profiler outfitted with pH and dissolved oxygen (DO) sensors, and a light transmissometer. Onboard sensors included two fluorometers (ultraviolet and chlorophyll), two automated Trace Metal Analyzers (TMA), an acoustic Doppler current profiler (ADCP), a digital fathometer, a differential global positioning system (DGPS) navigation receiver, and a Cu ion selective electrode (Cu-ISE). Vertical profiles were performed for every other box segment; otherwise, all sampling was performed at a depth of about 2 m.

Composite samples were collected from surface waters in San Diego Bay. These were collected from each of the box regions shown in the map in Figure 5 by continuously pumping into precleaned, 20-liter carboys. At the end of the transit through each box, subsamples were collected from the carboy for measurement of each of the parameters required.

Analyses were performed for those environmental parameters that define physical, chemical, biological and toxicological characteristics of any coastal embayment, including date, time of sampling, temperature, pH, light transmission, salinity, density, DO, Cu^{2+} , pH2 Cu and zinc concentrations measured with the TMA, Cu_{tot} , Cu_{diss} , zinc, total suspended solids (TSS), bacterial production, DOC, alkalinity, total CO_2 , chlorophyll, phaeopigments, bacterial abundance, cyanobacteria abundance, nitrates, phosphates, silicates, nitrites, ammonia, Cu complexation capacity, toxicity testing, and characteristics of organic ligands. Analytical procedures include those mentioned in Section 4.6, with the remaining procedures explained by Blake et al. (2004), Chadwick et al. (2004), Boyd et al. (2005), Rivera-Duarte and Zirino (2004), Rivera-Duarte et al. (2005) and Rosen et al. (2005).

In contrast to the approach followed in the demonstration in San Diego Bay, the demonstration at Pearl Harbor only includes preliminary calibration and validation of the integrated model. The data from San Diego Bay on the Cu accumulation by larvae of two sensitive organisms was used in the seawater-BLM and applied directly to Pearl Harbor. Both the calibration and validation were done directly with the internally integrated model.

The data from the Copper Water Compliance Studies at PHNS&IMF was used in this demonstration (Earley et al., 2007). The sampling and analysis plan for these studies included four sampling events, covering the dry and wet seasons. At each of these events a total of eight stations were sampled at about 1 m deep. The sampling parameters that were covered in ambient waters from Pearl Harbor include hydrographic, chemical, and toxic characteristics that are essential for the development of WER and Translator studies. Thus, while there may be some limited data collection requirements for this project, the majority of the calibration and validation data were from existing data sets, minimizing the costs to the project.

4.6 ANALYTICAL PROCEDURES

An extensive suite of parameters are required for the characterization of a DoD harbor for determination of WER, TMDL and for setting up a fate and effects and seawater-BLM model. However, among these parameters the following seem to be the most relevant for the modeling: Cu_{tot} , Cu_{diss} , Cu^{2+} , total organic carbon (TOC), DOC, TSS, salinity, and alkalinity as well as toxicity testing. The preferred analytical methods for the measurement of these parameters as well as those for the parameters required for the determination of the Cu accumulation by larvae of sensitive organisms are described in Appendix B, Analytical Methods Supporting the Experimental Design, of the technical report. These methods include the following: Method 7211, Cu by atomic absorption, furnace technique (USEPA, 1992); Method 1669, sampling ambient water for trace metals at EPA WQC levels (USEPA, 1996); Cu^{2+} with Cu-ISE (Rivera-Duarte and Zirino, 2004); TOC and DOC (Qian and Mopper, 1996); alkalinity (Hernández-Ayón et al., 1999); and chronic toxicity (USEPA, 1995).

This page intentionally left blank.

5.0 PERFORMANCE ASSESSMENT

5.1 PERFORMANCE DATA

The performance of the integrated CH3D/seawater-BLM for prediction of WQS in DoD harbors, is based in direct comparison to field measurements. The field data provides information on the environmental, toxicological, and hydrological characteristics in each harbor that is predicted by the integrated model. The different modeling components of the integrated model are first used separately to predict those characteristics. The final approach was to use the complete integrated model to predict the characteristics for unmodeled data. The performance data required for this exercise is shown in Table 2.

Table 2. Performance Data for the Demonstration of the Integrated Model.

Performance Topic	Type of Information
Concentration gradients and speciation of environmental parameters (i.e., Cu, DOC, etc.)	<ul style="list-style-type: none">• Environmental characteristics of the harbor
Toxicity assessment	<ul style="list-style-type: none">• Toxicological characteristics of the harbor
Hydrological assessment	<ul style="list-style-type: none">• Physical characteristics of the harbor
CH3D objectives	<ul style="list-style-type: none">• Reliability in predicting F&T of environmental parameters
Seawater-BLM objectives	<ul style="list-style-type: none">• Reliability in predicting toxicological characteristics
Integrated model objectives	<ul style="list-style-type: none">• Reliability in predicting measured environmental parameters• Reliability in predicting toxicological parameters• Reliability in predicting measured regulatory parameters• Operational time to accomplish these predictions• Stability of model• Reliability in predicting effects of discharge management in harbor

5.2 PERFORMANCE CRITERIA

The performance of the integrated model was assessed following the criteria shown in Table 3. The primary criteria follow the statistical comparison described in the performance objectives (Table 1). Our personnel evaluated the secondary criteria from observations. The integrated CH3D/seawater-BLM model runs with no stability problems; the model is 100% stable. The improvement in running time from the external to the internal mode is obvious. In external mode, once the CH3D finishes a run, the data is processed and provided to the seawater-BLM, this process takes from two to three days. In the internal mode, the data is transferred automatically from the CH3D to the seawater-BLM in a matter of seconds. However, the time for running each independent model remains the same in either mode.

Table 3. Performance Criteria and Confirmation Methods for the Demonstration of the CH3D/Seawater-BLM.

Performance Criteria	Expected Performance (pre demo)	Performance Confirmation Method	San Diego Bay Actual (post demo)	Pearl Harbor Actual (post demo)
PRIMARY CRITERIA (Performance Objectives) (Qualitative)				
PRIMARY CRITERIA (Performance Objectives) (Quantitative)				
Reliability of CH3D model prediction	The model should explain $\geq 60\%$ of the variance in the field data for Cu_{tot}	Comparison of measured and modeled Cu_{tot} distributions	Yes, explain 74% to 93% of variance	Yes, explain 61% to 94% of variance
Reliability of CH3D model prediction	The model should explain $\geq 60\%$ of the variance in the field data for Cu_{diss}	Comparison of measured and modeled Cu_{diss} distributions	Yes, explain 68% to 92% of variance	Yes, explain 68% to 92% of variance (when $\Delta C > 0.22 \mu g L^{-1}$)
Reliability of seawater-BLM prediction	The model should predict values in the same order of magnitude as the field data for Cu^{2+}	Comparison of measured and predicted Cu^{2+} values	Yes, 97% are within an order of magnitude	No, there are no available <i>in situ</i> Cu^{2+} measurements
Reliability of seawater-BLM	The model should predict the field data for toxicity within a factor of two	Comparison of measured and modeled Cu toxicity distributions	Yes, for 87% or better of the predicted values	Yes, for 83% or better of the predicted values
Reliability of integrated model	The model should predict the field data for WER within a factor of two	Comparison of field data with modeled WER distributions	Yes, 80% are within this range	Yes, 98% are within this range
SECONDARY CRITERIA (Performance Objectives) (Qualitative)				
Stability of integrated model	Integrated model should be 100% stable	Stability of integrated model to complete repetitive runs	Yes, model is 100% stable	Yes, model is 100% stable
Time optimization of integrated model	Integrated model should be 30% faster than parallel running of models	Measurement and optimization of time for computation	Yes, faster by up to three days	Yes, faster by up to three days

The calibration and validation of the CH3D, seawater-BLM and the integrated models were done by comparison with field data generated in previous efforts. This was accomplished with scatter plots, having the measured field data plotted as independent variable in the abscissa (x-axis), and the modeled data plotted as dependent variable in the ordinate (y-axis) (USEPA, 2006). These plots were used to evaluate the degree of correlation between the model predictions and the actual data, and to estimate the percentage of the variability of the field data that could be explained by the model.

In those cases where the independent variable (i.e., the measured data) has a minimal gradient (i.e., constant value), then use of correlation is not possible. This is the case for Cu^{2+} in San Diego Bay. A direct comparison between measured and predicted data was applied to verify if

they are within an order of magnitude. Note that the concentrations of Cu^{2+} are in the range from 1×10^{-13} to 1×10^{-12} M in San Diego Bay; therefore, a similitude within an order of magnitude is a relatively small range.

5.3 DATA ASSESSMENT

The rationale for selecting a performance objective of 60% (variance explained) for the prediction of environmental characteristics in the harbors is based on professional judgment from previous modeling efforts. For example, Chadwick et al. (2004) report similar comparisons between field data and modeled predictions for Cu_{tot} , Cu_{part} and Cu_{diss} that explain 91%, 73%, and 88% of the variance in the field data, respectively. The same data were used for the evaluation of the performance of the integrated model, and similar metrics were expected. This performance objective is affected by the propagation of errors occurring throughout the modeling. These errors arise from uncertainties in the quantification and prediction of source strength, water levels, water velocities, partitioning, and sediment exchange, among other factors. The highest precision is observed when physical parameters such as tides and currents, are modeled. Precision declines when less precise parameters, such as sources and sinks, are included. The inclusion of chemical parameters further decreases the precision of the prediction.

The integrated model fulfills the performance criteria for Cu_{tot} . In the case of Cu_{diss} , the performance can not be assessed in those cases where there is a lack of a gradient in concentration. However, there is a great similarity between predicted and measured data in all cases. The small range in variation of Cu^{2+} observed in San Diego Bay promoted the use of direct comparison to evaluate the similitude at the order of magnitude of the data. Predicted and measured Cu^{2+} is in the same order of magnitude for most of the bay, excluding the mouth. These results attest to the capability of the integrated model to predict environmental characteristics.

Comparison between measured and predicted toxicity data was based on the USEPA accepted range of two for these predictions. The acceptance of this factor of two is from results of toxicity testing done by the USEPA Environmental Research Laboratory, Duluth, Minnesota, in waters of Lake Superior, with the same species throughout a whole calendar year (Erickson et al., 1987). Results from these studies indicate that under the best prediction scenario, it is only possible to predict toxicity within a factor of two (Figure 7). Experience with the freshwater-BLM is that predictions within a factor of two are achievable when the model is properly parameterized and uses the water quality characteristics of the toxicity test water. This level of certainty has been sufficient for regulatory acceptance of the freshwater-BLM (USEPA, 2007).

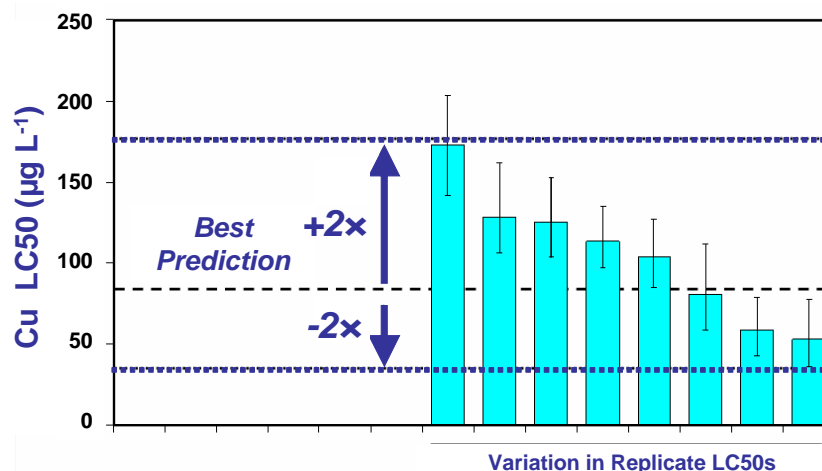


Figure 7. Measured (blue columns) and Best Prediction Range for Cu Toxicity (LC50) in Waters of Lake Superior (Erickson et al., 1987).

The integrated model provides predicted toxicities that are very comparable to the measured ones. For the two harbors, 83% of the predicted EC50s for *Mytilus galloprovincialis* were within a factor of two of reported values. For *Crassostrea gigas*, this value was 92%, while all predictions were within a factor of two of reported values for *Strongylocentrotus purpuratus* and *Dendraster excentricus*. One of the advantages of the integrated CH3D/seawater-BLM model is the prediction of high resolution (≈ 100 m) spatial distributions of parameters of regulatory concern, including toxicity threshold (EC50) and WER, which contrasts with the demanding effort required for measuring toxicity in enough samples to provide similar spatial distribution.

The predicted distributions of threshold toxicity values show the need to resolve spatial distributions of DOC. Spatial distributions of the toxicity threshold factor EC50 indicate a gradient in this parameter. These distributions are predicted by modeling DOC as having a spatially uniform production that gives average concentrations from the measurements. Therefore, the spatial distribution of DOC is averaged in the geographic regions in the bay. Further improvement in the resolution of DOC distributions will provide better refinement in the prediction of WQS.

The whole body LA50 was used in conjunction with the data of TSS, DOC, pH, and salinity in the integrated model to derive predicted WER for San Diego Bay and Pearl Harbor. The reference water composition was taken as the mean of coastal samples from the Scripps Institute of Oceanography and from the University of California Davis Marine Pollution Studies Laboratory at Granite Canyon (a total of nine samples). DOC measurements in these reference waters used in the toxicity tests averaged around 1.5 mg C L^{-1} . While this value may have been appropriate for comparison with those tests, it is somewhat higher than comparable reference waters. For example, in recent work for San Francisco Bay, the DOC concentrations in Granite Canyon reference waters ranged from 0.3 to 0.8 mg L^{-1} (Arnold et al., 2005). For this application, if the WER values were based on BLM predictions using reference water with lower DOC concentrations, all of the WER values would be higher, and it is unlikely that any would be below 1.0. The sensitivity of WER values to reference water chemistry is a clear disadvantage of the WER methodology.

Geometric mean WERs were slightly higher for San Diego Bay (1.479) than they were for Pearl Harbor (1.172). The geometric mean Cu_{diss} WER for the San Diego Bay (1.479) is slightly smaller than the range of 1.54 to 1.67 calculated by Rosen et al. (2005). The WER for Pearl Harbor (1.172) is also smaller than the WER (1.40) reported by Earley et al. (2007). The integrated CH3D/seawater-BLM model provides high-resolution prediction of WQS specific for the bay. There is a gradient in the predicted Cu_{diss} WERs in San Diego Bay going from values of about 1.4 by the mouth of the bay to values around 2.0 in the back of the bay. This compares well with the geographic distribution reported by Rosen et al. (2005), with lower values (geometric mean 1.26) in the North Bay and larger WERs (geometric mean 1.90) in the back of the bay. The comparison between predicted and measured Cu_{diss} WERs for the two DoD harbors shows that 88% of the values are within a factor of two of the measured values.

Implementation of WER predicted by the integrated CH3D/seawater-BLM model should provide regulatory relief while still achieving the level of protection intended by the WQC guidelines. Figure 8 shows the predicted levels of Cu_{diss} , the current WQC, and the level of relief provided by applying site-specific WQS in San Diego Bay. This figure also includes the margin of safety (MOS) predicted for the Bay. The MOS is the factor by which the predicted Cu_{diss} must be increased in order to reach the site-specific WQS. The area affected by tidal flushing and inputs from the adjacent coastal waters provides more complexing capacity and dilution to the sources of copper, as indicated by MOS values between 7 in box 2 to 4.0 in box 10 (Figure 8). The natural complexation capacity and dilution of the inputs provides a MOS value of 2.2 ± 0.5 for the rest of the bay. These results attest to the importance of adopting the integrated model for designation of environmental quality regulations, as it provides high-resolution geographic distributions of WQS and other important regulatory factors. It also shows that ambient Cu concentrations are close to current marine WQC of $3.1 \mu\text{g L}^{-1}$. However, when bioavailability is considered in the development of site-specific criteria in the Bay, the current copper concentrations are well below the criteria values with an MOS of at least $2\times$ throughout the bay.

The integrated model provides harbor-wide environmental and toxicological characteristics, and regulatory parameters that are comparable to those obtained by current methods. This demonstration provides evidence of the capability of the integrated model to predict these characteristics and parameters and substantiates the similitude of these predicted values with measured ones. USEPA is aware of this capability and is in the process of supporting the inclusion of the seawater-BLM into a full-strength seawater regulation.

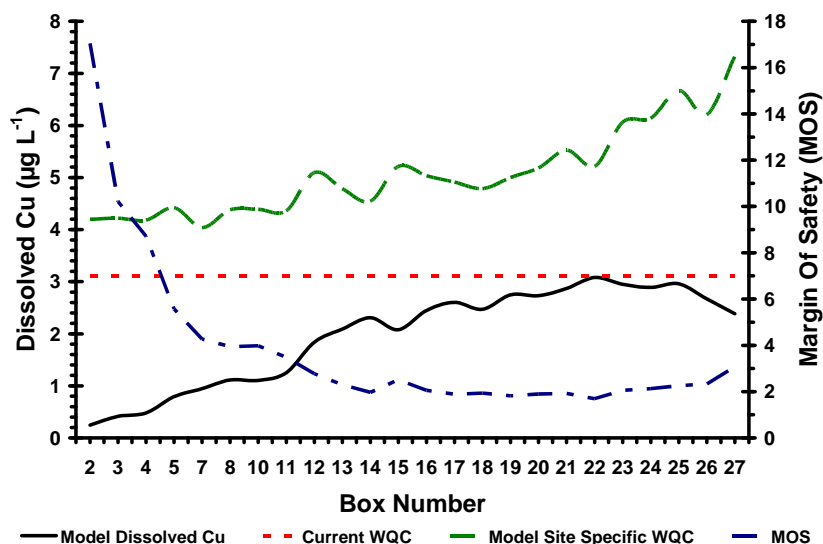


Figure 8. Relief Predicted by the Integrated CH3D/Seawater-BLM Model with a Site-Specific WQC for San Diego Bay.

(The margin of safety [MOS] is the \times -fold increase in Cu_{diss} required to reach the toxicity threshold.)

5.4 TECHNOLOGY COMPARISON

Field-developed WER is the alternative existing process. This includes sampling, measuring quality parameters, and testing toxicity. Demonstration of the integrated model was based on comparison with field-developed WER for both harbors. As indicated above, the WER field data was already available for San Diego Bay (Rosen et al., 2005) as well as for Pearl Harbor (Earley et al., 2007). And the performance data and criteria presented above are based on this comparison.

6.0 COST ASSESSMENT

6.1 COST REPORTING

The analysis and reporting of the costs associated with the development of the integrated model in San Diego Bay and Pearl Harbor were done by tracking costs and comparing them with those associated with the development of a WER and an F&T model (CH3D) in another DoD harbor with similar dimensions and characteristics as San Diego Bay. These analyses and reporting could not follow the Environmental Cost Analysis Methodology developed by the National Defense Center for Environmental Excellence (NDCEE, 1999). The actual costs incurred in the development of the San Diego Bay integrated CH3D/seawater-BLM model are shown in Table 4. Table 5 and Table 66 represent costs predicted for the application and development of CH3D and a WER in a harbor with similar dimensions and characteristics than San Diego Bay. These tables follow the Federal Remediation Technologies Roundtable guidance (FRTR, 1998).

The actual costs incurred in the demonstration of the San Diego Bay integrated CH3D/seawater-BLM model (Table 4) are categorized according to tasks required for the demonstration. The section on Operation and Maintenance is included for guidance; however, no actual costs are associated to this section, as the demonstration required a single validation of the integrated model. Funding for presentation and discussion of the use of the seawater-BLM for regulatory purposes is included to promote the acceptance of this model by USEPA. The total cost for the demonstration in San Diego Bay is \$580,000.

Table 4. Actual Costs Incurred in the Development and Application of an Integrated CH3D/BLM Model for San Diego Bay.

Cost Category	Subcategory	Cost
FIXED COSTS		
1. CAPITAL COSTS	Planning/preparation*	\$34,800
	Set-up of CH3D	\$21,667
	Bioaccumulation studies	\$32,500
	Materials/consumables**	\$24,750
	Calibration of CH3D	\$33,000
	Validation of CH3D	\$62,500
	Set-up of seawater-BLM	\$45,000
	Calibration of seawater-BLM	\$45,000
	Validation of seawater-BLM	\$45,000
	Integration CH3D + seawater-BLM	\$48,750
	Calibration of integrated model	\$66,000
	Validation of integrated model	\$62,500
	Other – management support	\$27,083
	Other – reporting	\$23,200
	Subtotal	\$571,750

*Labor was estimated at the rate for a federally employed scientist in FY08 of \$104.86. The same rate is applied in the following tables.

**These include materials used for copper larval bioaccumulation studies and analysis of samples.

Table 4. Actual Costs Incurred in the Development and Application of an Integrated CH3D/BLM Model for San Diego Bay (continued).

Cost Category	Subcategory	Cost
VARIABLE COSTS		
2. OPERATION AND MAINTENANCE	Integrated model run	(\$16,500)
	Model/document maintenance	(\$5,417)
	Reporting requirements	(\$11,600)
	Subtotal	\$0
3. OTHER TECHNOLOGY - SPECIFIC COSTS	Presentation/discussion for regulatory enforcement	\$8,250
	Subtotal	\$8,250
TOTAL TECHNOLOGY COST		\$580,000

The costs for implementation of an F&T model (CH3D, Table 5) are used for comparison with developing the integrated model. The integrated model provides a geographic distribution of toxicity and regulatory standards in the harbor. Similar distributions can be achieved by implementing a WER and an F&T model separately and combining the results from each model generating the same information. Therefore, the costs of this technology demonstration are compared to the costs expected for the applications of these two combined efforts. The costs for implementing the CH3D in a harbor with similar size and characteristics as San Diego Bay are calculated at \$128,384 (Table 5).

Table 5. Costs Expected for the Development and Application of CH3D Model in a New Harbor.

Cost Category	Subcategory	Cost
FIXED COSTS		
1. CAPITAL COSTS	Planning/preparation	\$11,600
	Set-up of CH3D	\$21,667
	Materials/consumables	\$2,475
	Calibration of CH3D	\$33,000
	Validation of CH3D	\$31,250
	Other – management support	\$5,417
	Other – reporting	\$11,600
	Subtotal	\$117,009
VARIABLE COSTS		
2. OPERATION AND MAINTENANCE	Reporting requirements	\$5,800
	Subtotal	\$5,800
3. OTHER TECHNOLOGY: SPECIFIC COSTS	Presentation/discussion for regulatory enforcement	\$5,575
	Subtotal	\$5,575
TOTAL TECHNOLOGY COST		\$128,384

The costs associated with the development of a WER for a harbor similar in size and characteristics to San Diego Bay (Table 66) include only those expected for toxicity testing and associated measurement of Cu concentrations. There is no set value associated with the number of stations for WER development, but federal guidance (USEPA, 2001) indicates that the stations selected should be representative of the body of water. The WER calculated by Rosen et al. (2005) for San Diego Bay are within a factor of three, suggesting that they are similar enough at both ends of the bay for regulatory purposes. However, if all samples in this study were

collected near the back of the bay, the site-specific criterion would not be protective of areas near the mouth of the bay. This information was used in calculating the costs for eight stations distributed throughout the bay and characterizing the toxicity (EC50) in two sampling events to distinguish between dry and wet seasons. These costs are based on the current procedure at the Space and Naval Warfare Systems Center Pacific (SSC-Pacific) for determination of EC50s, with seven different Cu concentrations in the aliquots for toxicity testing in each sample. Costs of measurement of Cu_{diss} and Cu_{tot} in each of these aliquots by inductively coupled plasma mass spectrometry (ICP-MS) by a commercial laboratory are used. Development of a WER following the USEPA recommended procedure (USEPA, 2001) in this hypothetical harbor is estimated at \$200,722.

Table 6. Costs Associated with Field Development of a WER for a DoD Harbor of Similar Dimensions as San Diego Bay.

(The predicted effort is for eight sampling stations, two sampling events [wet and dry seasons] and includes only the costs required for determination of toxic points (EC50), without any further biological, physical or chemical characterization of the bay.)

Cost Category	Subcategory	Cost
FIXED COSTS		
1. CAPITAL COSTS	Planning/preparation	\$15,000
	Sampling*	\$4,000
	Toxicity testing	\$40,000
	Chemical measurements (Cu _{diss})	\$28,000
	Chemical measurements (Cu _{tot})	\$28,000
	Other – management support	\$3,000
	Other – reporting	\$8,389
	Subtotal	\$126,389
VARIABLE COSTS		
2. OPERATION AND MAINTENANCE	Labor	\$29,361
	Vessel rental/maintenance	\$6,000
	Laboratory maintenance	\$3,000
	Result analysis	\$8,389
	Model / document maintenance	\$4,194
	Reporting requirements	\$8,389
	Subtotal	\$59,333
3. OTHER TECHNOLOGY: SPECIFIC COSTS	Presentation/discussion for regulatory enforcement	\$15,000
	Subtotal	\$15,000
TOTAL TECHNOLOGY COST		\$200,722
Unit cost per sample		\$12,545

*Costs include vessel rental, sampling materials, labor for sampling. Samples are surficial harbor seawater.

The total costs for independent implementation of a WER and an F&T model for a harbor of similar dimensions and characteristics as San Diego Bay is estimated at \$329,106 (Table 8), which is \$250,894 less than the costs incurred in the development and demonstration of the integrated model in San Diego Bay (Table 8). The costs for implementation of the integrated model in a harbor of similar dimensions and characteristics as San Diego Bay is estimated at \$189,368 (Table 7), which is \$139,937 less than an independent implementation of a WER and an F&T model (Table 8). If the user selects only the application of the seawater-BLM, the total

estimated cost would be \$60,984. The cost estimate for implementing the integrated model assumes that ancillary data required for the CH3D and seawater-BLM models are available. Sampling and analysis for these parameters will increase the projected costs.

Table 7. Costs Estimated for the Implementation of the Integrated CH3D/Seawater-BLM Model in Another DoD Harbor.

Cost Category	Subcategory	Cost
FIXED COSTS		
1. CAPITAL COSTS	Planning/preparation	\$23,200
	Set-up of CH3D	\$21,667
	Materials/consumables	\$2,475
	Integrated model se-up/run	\$21,667
	Calibration of integrated model	\$33,000
	Validation of integrated model	\$31,250
	Other – management support	\$5,417
	Other – reporting	\$11,600
	Subtotal	\$150,276
VARIABLE COSTS		
2. OPERATION AND MAINTENANCE	Integrated model run	\$16,500
	Model/document maintenance	\$5,417
	Reporting requirements	\$11,600
	Subtotal	\$33,517
3. OTHER TECHNOLOGY: SPECIFIC COSTS	Presentation/discussion for regulatory enforcement	\$5,575
	Subtotal	\$5,575
TOTAL TECHNOLOGY COST		\$189,368

Table 8. Summary of Costs Incurred for the Demonstration in San Diego Bay (actual), and for Implementation of Different Models in a Harbor Similar to San Diego Bay.

Activity	Cost (\$)	Cost Difference
Demonstration San Diego Bay (actual)	\$580,000	
Difference actual San Diego Bay – (CH3D + WER)		\$250,894
Implementation of F&T model CH3D in New Harbor	\$128,384	
Implementation of WER in New Harbor	\$200,722	
Total expected costs CH3D + WER	\$329,106	
Implementation of Integrated model in New Harbor	\$189,368	
Difference (CH3D + WER) – Integrated Model		\$139,957
Implementation of seawater-BLM in New Harbor	\$60,984	

6.2 COST ANALYSIS

The major cost drivers for implementing the integrated model are on setting up and calibrating the models, which are fixed costs. These procedures are required to ensure that the information predicted is realistic for the harbor conditions. Once the integrated model is calibrated, minimum costs are required for operation and maintenance (\$33,517, Table 7). The integrated model allows for modification and improvement on the F&T and toxicity prediction capabilities and should evolve and mature with harbor conditions. In addition to being a tool for WQS estimation and verification, the integrated model helps on the allocation of best management

practices on sources and can forecast the resulting effects in the harbor. These expected savings are difficult to predict, as they vary among harbors.

Costs associated with eliminating regulatory fines by implementing attainable WQS with the integrated model are similar to those provided by implementing a WER. The main savings with the integrated model are related to the higher spatial and temporal resolution of environmental parameters and the ability to use the model as a management tool for regulatory control.

This page left blank intentionally.

7.0 IMPLEMENTATION ISSUES

7.1 COST OBSERVATIONS

The costs of implementation of the integrated CH3D/seawater-BLM in a new harbor are expected to be one-third of the costs of the demonstration of the model in San Diego Bay. Some of this decrease in costs is reflected by the elimination of some tasks (i.e., Cu bioaccumulation study, external and internal calibrations, etc.) that are not required for implementation in another harbor. While the integrated model remains a “living” document, allowing for improvement and changes, the model is ready for implementation in other harbors. However, costs associated with availability of data on environmental parameters required for this implementation and information on toxic characteristics that are highly desirable could increase the costs of implementation in other harbors.

7.2 PERFORMANCE OBSERVATIONS

The performance criteria followed in this demonstration were used to provide information on the efficacy of the integrated CH3D/seawater-BLM model to predict temporal and spatial distributions of environmental and toxicological parameters. Two different criteria were used, depending on the presence of a ΔC . A correlation between predicted and measured concentration was used in those cases where there is a ΔC . Direct comparison in the magnitude of the values or concentrations was followed in the cases where the parameter had a constant value (i.e., no ΔC) throughout the harbor. These criteria were fulfilled in their respective application, and indicate that the model predicts realistic environmental and toxicological temporal and spatial distributions.

Secondary criteria addressed the computational stability and speed of the integrated model. These characteristics were evaluated from observations by our personnel, and show that the model is running at good computational standards of stability and speed. These standards are evolving with the development of faster computer systems, and use of these systems should improve the response by the integrated model.

7.3 SCALE UP

This demonstration was run at full-scale implementation and the costs and performance criteria reported are for full-scale conditions.

7.4 OTHER SIGNIFICANT OBSERVATIONS

Estuarine conditions have not been addressed for the application of the BLM. The freshwater-BLM has already been incorporated into a freshwater WQC (USEPA, 2007), and application of the integrated model in marine (i.e., full-strength seawater) harbors is covered in this demonstration. However, research is required for the situation in an estuary, where fresh river water mixes with saltwater in a continuous flow to the ocean. Implementation of an integrated F&T/BLM model in estuarine situations should cover most of the possible conditions expected in coastal areas.

7.5 LESSONS LEARNED

There are two characteristics that require previous and continued improvement of the integrated model. There is the need for environmental and toxicological data for successful implementation of the model. This requirement could only be fulfilled with actual sampling and analysis following recommended procedures. Once the model is implemented, it is amenable for improvement, by incorporation of better information. One of the sources of this information is improved efforts on the characterization of environmental, toxicological and source parameters. This also requires sampling and analysis following the best procedures available. Therefore, implementation and optimization of the integrated model is dependant on the best information available at any time.

7.6 END-USER ISSUES

This demonstration contributes to the transition of this technology to the user community by providing a clear example of implementation at real-world DoD sites. Critical aspects of this contribution include development and refinement of the BLM for sensitive saltwater toxicity endpoints and implementation of USEPA guidance for TMDL and site-specific WQS within a rigorous numerical modeling framework for copper and eventually other metals. Potential users will have the opportunity to find out the level of relief potentially achievable with a WER study, at a more affordable price. In addition, the developed integrated model will provide the capability to evaluate for the best possible remedial action in case of exceeding standards.

7.7 APPROACH TO REGULATORY SUSTAINABLE INFRASTRUCTURE AND ACCEPTANCE

This demonstration included direct presentation/discussion with the USEPA on inclusion of a seawater-BLM in WQC regulation. Results from the demonstration were presented in two separate meetings to the USEPA, Office of Water, Office of Science and Technology, Health and Ecological Criteria Division at the USEPA headquarters in Washington, D.C. These meetings were promoted by Ray Arnold. Results from the final calibration and validation of the seawater-BLM were presented on the meeting of April 14, 2008, where it was accepted that the seawater-BLM is ready for inclusion for full-strength seawater regulation. The final procedures for this inclusion are expected to be completed by December 2008. A draft document for the inclusion of the seawater-BLM for regulatory use could be achieved by 2010.

8.0 REFERENCES

- Arnold, W.R. 2005. *Effects of dissolved organic carbon on copper toxicity: Implications for saltwater copper criteria*. Integrated Environmental Assessment and Management 1: 34-39.
- Arnold, W.R., R.C. Santore, and J.S. Cotsifas. 2005. *Predicting copper toxicity in estuarine and marine waters using the Biotic Ligand Model*. Marine Pollution Bulletin 50: 1634-1640.
- Arnold, W.R., J.S. Cotsifas, and K.M. Corneillie. 2006. *Validation and update of a model used to predict copper toxicity to the marine bivalve Mytilus sp.* Environmental Toxicology 21: 65-70.
- Bielmyer, G.K., M. Grosell, P.R. Paquin, R. Mathews, K.-B. Wu, R.C. Santore, and K.V. Brix. 2007. *Validation study of the acute biotic ligand model for silver*. Environmental Toxicology and Chemistry 26(10): 2241-2246.
- Blake, A.C., D.B. Chadwick, A. Zirino, and I. Rivera-Duarte. 2004. *Spatial and temporal variations in copper speciation in San Diego Bay*. Estuaries 25(3): 437-447.
- Boyd, T.J., D.M. Wolgast, I. Rivera-Duarte, O. Holm-Hansen, A. Zirino, and D.B. Chadwick. 2005. *Effects of dissolved and complexed copper on heterotrophic bacterial production in San Diego Bay*. Microbial Ecology 49(3): 353-366.
- Campbell, P.G.C. 1995. "Interactions Between Trace Metals and Aquatic Organisms: A Critique of the Free-ion Activity Model." Chapter 2 in Metal Speciation and Bioavailability in Aquatic Systems, A. Tessier and D.R. Turner, eds., IUPAC, John Wiley and Sons, New York, pp. 45-102.
- Chadwick, D.B., A. Zirino, I. Rivera-Duarte, C.N. Katz, and A.C. Blake. 2004. *Modeling the mass balance and fate of copper in San Diego Bay*. Limnology & Oceanography 49(2): 355-366.
- Chadwick, D.B., and J.L. Largier. 1999a. *Tidal exchange at the bay-ocean boundary*. Journal of Geophysical Research, 104(C12): 29901-29924.
- Chadwick, D.B., and J.L. Largier. 1999b. *The influence of tidal range on the exchange between San Diego Bay and the ocean*. Journal of Geophysical Research, 104(C12): 29885-29899.
- Di Toro, D.M., H.E. Allen, H.L. Bergman, J.S. Meyer, P.R. Paquin, and R.C. Santore. 2001. *Biotic ligand model of the acute toxicity of metals, 1. Technical basis*. Environmental Toxicology and Chemistry 20(10): 2383-2396.
- Earley, P.J., G. Rosen, I. Rivera-Duarte, R.D. Gauthier, J. Thompson, and B. Swope. 2007. *A Comprehensive copper compliance strategy: Implementing regulatory guidance at Pearl Harbor Naval Shipyard & Intermediate Maintenance Facility*. SSC-SD,

Technical Report 1952, San Diego, California.
<http://www.spawar.navy.mil/sti/publications/pubs/index.html>.

- Esser, B.K., and A. Volpe. 2002. *At-sea high-resolution trace element mapping: San Diego Bay and its plume in the adjacent coastal ocean*. Environmental Science & Technology 36(13): 2826-2832.
- Erickson, R.J., D.A. Benoit, and V.R. Mattson. 1987. *A prototype toxicity factors model for site-specific copper water quality criteria*. U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth, Minnesota. (Revised September 5, 1996).
- Federal Remediation Technologies Roundtable. 1998. *Guide to documenting and managing cost and performance information for remediation projects (Revised version)*. EPA-542-B-98-009. October 1998. <http://www.ftr.gov>.
- Flegal, A.R., and S. Sañudo-Wilhelmy. 1993. *Comparable levels of trace metal contamination in two semi-enclosed embayments: San Diego Bay and South San Francisco Bay*. Environmental Science & Technology 27(9): 1934-1936.
- Hawaii State Department of Health. 2004. *Final 2004 List of Impaired Waters in Hawaii*. Prepared under the Clean Water Act Section 303(d) by Hawaii State Department of Health Environmental Planning Office, 67 pp.
- Hernández-Ayón, J.M., L.S. Belli, and A. Zirino. 1999. *pH, alkalinity and total CO₂ in coastal seawater by potentiometric titration with a difference derivative readout*. Analytica Chimica Acta 394(1): 101-108.
- Johnson, B.H., K.W. Kim, R.E. Heath, B.B. Hsieh, and H.L. Butle. 1991. *Development and verification of a three-dimensional numerical hydrodynamic, salinity, and temperature model of Chesapeake Bay*. Technical Report HL-91-7, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.
- Johnson, B.H., H.V. Wang, and K.W. Kim. 1995. *Can numerical estuarine models be driven at the estuary mouth?* In: Estuarine and Coastal Modeling, Proceedings of the 4th International Conference, American Society of Civil Engineers, San Diego, California, October 26-28, 1995. M.L. Spaulding and R.T. Cheng, eds., pp. 255-267.
- Johnson, H.D., J.G. Grovhoug, and A.O. Valkirs. 1998. *Copper loading to U.S. Navy harbors*. SSC-SD Technical Document 3052.
- Katz, C.N. 1998. *Seawater Polynuclear Aromatic Hydrocarbons and Copper in San Diego Bay*. SSC San Diego Technical Document 1768, San Diego, California.
- Morel, F.M. 1993. *Complexation. Trace Metals and Microorganisms*. In: F.M.M. Morel and J.G. Hering, eds., Principles and Applications of Aquatic Chemistry, Chapter 6, Wiley Interscience, New York, pp. 405-414.

- National Defense Center for Environmental Excellence. 1999. *Environmental Cost Analysis Methodology (ECAM) Handbook*. March 29, 1999. URL: <http://www.estcp.org>.
- Nriagu, J.O. 1996. *A History of Global Metal Pollution*, Science 272:223-224.
- Paquin, P.R., J.W. Gorsuch, S. Apte, G.E. Batley, K.C. Bowles, P.G.C. Campbell, C.G. Delos, D.M. Di Toro, R.L. Dwyer, F. Galvez, R.W. Gensemer, G.G. Goss, C. Hogstrand, C.R. Janssen, J.C. McGeer, R.B. Naddy, R.C. Playle, R.C. Santore, U. Schneider, W.A. Stubblefield, C.M. Wood, and K.B. Wu. 2002a. *The biotic ligand model: a historical overview*. Comparative Biochemistry and Physiology Part C 133: 3–35.
- Paquin, P.R., V. Zoltay, R.P. Winfield, K.B. Wu, R. Mathew, R.C. Santore, and D.M. Di Toro. 2002b. *Extension of the biotic ligand model of acute toxicity to a physiologically-based model of the survival time of rainbow trout (Oncorhynchus mykiss) exposed to silver*. Comparative Biochemistry and Physiology Part C 133: 305–343.
- Paquin P.R., R. Bell, G. Bielmyer, K.V. Brix, M.J. Grosell, R. Mathew, R. Naddy, A. Redman, R.C. Santore, S. Smith, and K.B. Wu. 2007. *Bioavailability and Effects of Ingested Metals on Aquatic Organisms*. Prepared for the Water Environment Research Foundation, WERF Project 99-TCR-1-2.
- PRC. 1997. *Report of copper loading to San Diego Bay, California*. Report to California Regional Water Quality Control Board, San Diego Region, 14 May 1997.
- Qian, J. G., and K. Mopper. 1996. *Automated high performance, high-temperature combustion total organic carbon analyzer*. Analytical Chemistry 68: 3090–3097.
- Rivera-Duarte, I., and A. Zirino. 2004. *Response of the Cu(II) ion selective electrode to Cu titration of artificial and natural shore seawater and measurement of the Cu complexation capacity*. Environmental Science & Technology 38(11): 3139-3147.
- Rivera-Duarte, I., G. Rosen, D. Lapota, D. B. Chadwick, L. Kear-Padilla, and A. Zirino. 2005. *Copper toxicity to larval stages of three marine invertebrates and copper complexation capacity in San Diego Bay, California*. Environmental Science & Technology 39(6): 1542-1546.
- Rosen, G., I. Rivera-Duarte, L. Kear-Padilla, and D. B. Chadwick. 2005. *Use of laboratory toxicity tests with bivalve and echinoderm embryos to evaluate the bioavailability of copper in San Diego Bay, California, USA*. Environmental Toxicology and Chemistry 24(2): 415-422.
- Rosen, G., I. Rivera-Duarte, D.B. Chadwick, A. Ryan, R. Santore, and P. Paquin. 2008. *Critical tissue copper residues for marine bivalve (Mytilus galloprovincialis) and echinoderm*. Marine Environmental Research. In press.

- Santore, R.C. and C.T. Driscoll. 1995. *The CHESS Model for Calculating Chemical Equilibria in Soils and Solutions, Chemical Equilibrium and Reaction Models*. SSSA Special Publication 42, Soil Society of America, American Society of Agronomy.
- Santore, R.C., D.M. Di Toro, P.R. Paquin, H.E. Allen, and J.S. Meyer. 2001. *Biotic ligand model of the acute toxicity of metals. 2. Application to acute copper toxicity in freshwater fish and Daphnia*. Environmental Toxicology and Chemistry 20(10): 2397–2402.
- Schiff, K. and D. Diehl. 2002. *Assessment of trace metal emissions from antifouling paints during underwater cleaning events and passive leaching*. International Congress on Marine Corrosion and Fouling, San Diego, California, 21-26 July 2002.
- Schiff, K., D. Diehl, and A. Valkirs. 2004. *Copper emissions from antifouling paint on recreational vessels*. Marine Pollution Bulletin 48: 371-377.
- Seligman, P.F. and A. Zirino. 1998. *Chemistry, Toxicity and Bioavailability of Copper and Its Relationship to Regulation in the Marine Environment*. Office of Naval Research First Workshop Report. SSC San Diego Technical Document 3044, San Diego, California.
- Seligman, P.F., A.O. Valkirs, J.S. Caso, I. Rivera-Duarte, and E. Haslbeck. 2001. *Copper release rates from antifouling marine coatings and their relationship to loading and toxicity in San Diego Bay, California*. In: Symposium on Pollution Prevention from Ships and Shipyards. Oceanology International 2001 Conference, Miami, Florida, April 4-5, 2001. M.A. Champ, ed., pp. 64-81.
- Shafer, M.M., S.R. Hoffman, J.T. Overdier, and D.E. Armstrong. 2004. *Physical and kinetic speciation of copper and zinc in three geochemically contrasting marine estuaries*. Environmental Science & Technology 38(14): 3810-3819.
- Sheng, P.Y., D.E. Eliason, X.-J. Chen, and J.-K. Choi. 1991. *A three-dimensional numerical model of hydrodynamics and sediment transport in lakes and estuaries: Theory, model development and documentation*. Report to U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia, 163 pp.
- Stephan, C.E., D.I. Mount, D.J. Hansen, J.H. Gentile, G.A. chapman, and W.A. Brungs. 1985. *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses*. PB85-227049. National Technical Information Service, Springfield VA.
- Tipping, E. 1994. *WHAM--A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances*. Computers and Geosciences 20(6): 973-1023.
- U.S. Environmental Protection Agency. 1992. *Method 7211: Copper by Atomic Absorption, Furnace Technique*. Revision 1, July 1992.

- U.S. Environmental Protection Agency. 1995. *Short-term methods for estimating the chronic toxicity of effluents and receiving waters to West Coast marine and estuarine Organisms. Section 15: Purple Urchin, Strongylocentrotus purpuratus and Sand Dollar, Dendraster excentricus Larval Development Test Method.* EPA/600/R-95/136.
- U.S. Environmental Protection Agency. 1996. *Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels.* January 1996.
- U.S. Environmental Protection Agency. 1997. *Water Quality Standards: Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California.* Proposed Rule. 40CFR Part 131. Federal Register 62:150. Washington, D.C.
- U.S. Environmental Protection Agency. 1999a. *Draft Guidance for Water-Quality-based Decisions: The TMDL Process (Second Edition).* EPA 841-D-99-001. Washington, D.C.
- U.S. Environmental Protection Agency. 1999b. *Phase I Uniform National Discharge Standards for Vessels of the Armed Forces.* Technical development document. EPA 821-R-99-001. Washington, D.C.
- U.S. Environmental Protection Agency. 2001. *Streamlined water-effect ratio procedure for discharges of copper.* EPA 822-R-01-005.
- U.S. Environmental Protection Agency. 2006. *Data Quality Assessment – Statistical Methods for Practitioners,* EPA QA/G-9S. EPA/240/B-06/003.
- U.S. Environmental Protection Agency. 2007. *Aquatic life ambient freshwater quality criteria – copper, 2007 Revision.* EPA-822-F-07-001.
- Valkirs, A.O., P.F. Seligman, E. Haslbeck, and J.S. Caso. 2003. *Measurement of copper release rates from antifouling paint under laboratory and in situ conditions: implications for loading estimation to marine water bodies.* Marine Pollution Bulletin 46: 763-779.
- Wang, H.V., B.H. Johnson, and C.F. Cerco. 1997. *The Chesapeake Bay experience.* In: Estuarine and Coastal Modeling, Proceedings of the Fifth International Conference. American Society of Civil Engineers, Alexandria, Virginia, October 22-24, 1997. M.L. Spaulding and A.F. Blumberg, eds., pp. 16-27.
- Wang, P.F. 1992. *Review of equations of conservation in curvilinear coordinates.* Journal of Engineering Mechanics 118(11): 2265-2281.
- Wang, P.F., and J.L. Martin. 1991. *Temperature and conductivity modeling for the Buffalo River.* Journal of Great Lakes Research 17(4): 495-503.
- Wang, P.F., and S.C. McCutcheon. 1993. *Note on estuary-river models using boundary-fitted coordinates.* Journal of Hydraulic Engineering 119(10): 1170-1175.

- Wang, P.F., and K. Richter. 1999. *A hydrodynamic model study using CH3D for Sinclair Inlet*. SSC-SD Technical Report to Puget Sound Naval Shipyard, 50 pp.
- Wang, P.F., R.T. Cheng, K. Richter, E.S. Gross, D. Sutton, and J.W. Gartner. 1998. *Modeling tidal hydrodynamics of San Diego Bay, California*. Journal of the American Water Resources Association 34(5): 1123-1140.
- Wood, C.M. 2001. "Toxic Responses of the Gill," Chapter 1 in *Target Organ Toxicity in Marine and Freshwater Teleosts, Volume 1 – Organs*," D. Schlenk and W.H. Benson, eds., Taylor and Francis, London and New York, pp. 1-89.
- Woodward-Clyde. 1996. *PAH waste load determinations for San Diego Bay*. Report to the California Regional Water Quality Control Board, San Diego Region and San Diego Bay Interagency Water Quality Panel.
- Zirino, A., and P.F. Seligman. 2002. *Copper chemistry, toxicity and bioavailability and its relationship to regulation in the marine environment*. Office of Naval Research Second Workshop Report. SSC-SD Technical Document 3140.
- Zirino, A., S. Lieberman, and C. Clavell. 1978. *Measurement of Cu and Zn in San Diego Bay by automated anodic stripping voltammetry*. Environmental Science & Technology 12(1): 73-79.

APPENDIX A

POINTS OF CONTACT

Point of Contact	Organization	Phone Fax E-Mail	Role
Dr. D. Bart Chadwick	SSC-Pacific, Code 71750 53475 Strothe Road San Diego, CA 92152-6325	Phone: (619) 553-5333 Fax: (619) 553-3097 E-Mail: bart.chadwick@navy.mil	Principal Investigator
Dr. Ignacio Rivera-Duarte	SSC-Pacific, Code 71750 53475 Strothe Road San Diego, CA 92152-6325	Phone: (619) 553-2373 Fax: (619) 553-6305 E-Mail: ignacio.rivera@navy.mil	Bioaccumulation, Administration
Dr. Pei-Fang Wang	SSC-Pacific, Code 71750 53475 Strothe Road San Diego, CA 92152-6325	Phone: (619) 553-9192 Fax: (619) 552-6305 E-Mail: pei-fang.wang@navy.mil	CH3D Model Integration
Mr. Ernie Arias	SSC-Pacific, Code 71750 53475 Strothe Road San Diego, CA 92152-6325	Phone: (619) 553-3579 Fax: (619) 553-6305 E-Mail: ernie.arias@navy.mil	Quality Assurance Officer
Mr. Gunther Rosen	SSC-Pacific, Code 71750 53475 Strothe Road San Diego, CA 92152-6325	Phone: (619) 553-0886 Fax: (619) 553-6305 E-Mail: gunther.rosen@navy.mil	Bioaccumulation
Mr. Robert C. Santore	HydroQual, Inc. 4914 West Genesee Street Camillus, NY 13031	Phone: (315) 484-6220 Fax: (315) 484-6221 E-Mail: rsantore@hydroqual.com	BLM Model Development and Integration
Mr. Paul Paquin	HydroQual, Inc. 1200 MacArthur Boulevard First Floor Mahwah, NJ 07430	Phone: (201) 529-5151 Fax: (201) 529-5728 E-Mail: ppaquin@hydroqual.com	BLM Model Development and Integration
Dr. Adam Ryan	HydroQual, Inc. 4914 West Genesee Street Camillus, NY 13031	Phone: (315) 484-6220 Fax: (315) 484-6221 E-Mail: aryan@hydroqual.com	BLM Model Development and Integration
Mr. William Swietlik	USEPA Office of Water, Health and Ecological Criteria Division 1200 Pennsylvania Avenue, NW Washington, D.C. 20406	Phone: (202) 566-1129 Fax: (202) 566-1139 E-Mail: swietlik@william@epa.gov	Regulatory Contact
Mr. Luis A. Cruz	USEPA Office of Water, Health and Ecological Criteria Division 1200 Pennsylvania Avenue, NW Washington, D.C. 20406	Phone: (202) 566-1095 Fax: (202) 566-1140 E-Mail: cruz.luis@epa.gov	Regulatory Contact
Dr. Andrea Leeson	ESTCP 901 N Stuart Street, Suite 303 Arlington, VA 22203	Phone: (703) 696-2118 Fax: (703) 696-2114 E-Mail: Andrea.Leeson@osd.mil	Program Manager



ESTCP Program Office

901 North Stuart Street
Suite 303
Arlington, Virginia 22203
(703) 696-2117 (Phone)
(703) 696-2114 (Fax)
e-mail: estcp@estcp.org
www.estcp.org